IMMOBILISATION OF COPPER, CHROMIUM AND ARSENIC ON STABILISED DOMESTIC REFUSE

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For three people who have had a profound influence on my life.
My father, Richard Ballard and my friends,
James G Petrie and Andrew J Pitt.

SYNOPSIS

The disposal of copper-chromium-arsenic, whether in solution or in combination with wood, has the potential to become a global problem. This chemical is commonly called CCA or Tanalith, and is classed as a waterborne wood preservative. Current global production of this class of chemicals is estimated at 90 000 tonnes $annum^{-1}$. In South Africa (1988), the production of preservative treated wood approximates 430 000 m^3annum^{-1} (UNEP, 1994).

An experimental study to assess of the capacity of landfill biomass to adsorb (and retain) copper, chromium and arsenic waste chemicals has been carried out at laboratory and pilot scale. The work is motivated by the desire to explore the potential of domestic landfill sites to act as a final depositories for hazardous chemicals at minimal environmental risk. Copper is present as the sulphate (copper (II)); chromium is present as dichromate (chromium (VI)); arsenic is present as the pentoxide (arsenic(V)). The laboratory scale investigation focused on the evaluation of kinetic rate constants (adsorption and desorption) and the evaluation of adsorption isotherms. At pilot-scale, the residence time distribution/deviation from ideal behaviour of the pilot-scale landfill columns was determined. Subsequently, the kinetic rate constants and the results from the residence time distribution studies were evaluated at pilot-scale. The final phase of the investigation was the application of the data obtained at laboratory and pilot-scale, to an assessment of full scale landfill practice.

The laboratory scale experiments were carried out at three pH levels; pH5.5, pH6.4 and pH7.0. The investigative method was a modification of the US EPA Method 1311 **T**oxicity **C**haracteristic **L**eaching **P**rocedure (TCLP) (USEPA, 1992). Freundlich Isotherms were successfully constructed for copper adsorption at the pH values of 5.5 and 7.0, and for chromium and arsenic adsorption at pH values of 5.5, 6.4 and 7.0. Adherence to the Freundlich isotherm is generally considered to indicate adsorption onto a heterogeneous surface. Values obtained for the Freundlich equilibrium distribution coefficient (K_F) may be considered as a measure of affinity between solute and adsorbent. Over the pH range of the laboratory studies, the degree of affinity of the metals with municipal solid waste was, copper > arsenic > chromium.

The rate of adsorption of all the metals onto the municipal solid waste was initially rapid and decreased with prolonged reaction time. A two-constant rate equation (or modified Freundlich equation) developed by Kuo and Lotse (1974) was found to successfully describe the rate of metallic ion adsorption. Researchers in the field of soil science have found that the use of the modified Freundlich equation indicates that reactions at the solid phase are associated with activated diffusional processes. Additional examination showed the data conformed to a generalised model indicative of heterogeneous adsorption. This confirmed the results from the equilibrium studies. The desorption of chromium was insignificant, approximating 1 percent, whilst the desorption of copper was less than 4 percent of that adsorbed. Arsenical desorption was more significant, it did, however, average less than 10 percent of the arsenic adsorbed. For this reason, the kinetics of

desorption were not investigated further, and attention was limited to a study of the adsorption kinetics.

Five pilot-scale landfill columns were constructed. The columns are 4m in height, 0.8m in diameter, and contain approximately 700kg of municipal solid waste. The solid waste was pulverised to between 25-40mm before placement; average bulk density of the municipal solid waste in the pilot-scale landfill columns was 922kgm^{-3}. Analysis of the solid waste and leachate produced indicated the solid waste to be completely stabilised. Tracer studies were undertaken at pilot-scale using lithium sulphate. Recovery of lithium was better than 92 percent. A solution of copper-chromium-arsenic was added to two of the pilot-scale columns and the effluent closely monitored. The results obtained at laboratory and pilot-scale were utilised to provide functional data that may be applied by the landfill practitioner. This was demonstrated by a specific case study.

The maximum amount of copper-chromium-arsenic solution that could be co-disposed with municipal solid waste was; copper at 67gtonne^{-1}; chromium at 195gtonne^{-1} and arsenic at 195gtonne^{-1}. The disposal ratio of these metals was dictated by the formulation of the CCA (Tanalith) wood preservative. Comparison was made of loading rates quoted by the **D**epartment **o**f the **E**nvironment (DOE) in the United Kingdom. In general, loading rates proposed from the experimental work and predicted by the modelling undertaken in this study, concurred with loading rates employed in the United Kingdom, recommended by the Department of the Environment.

It is hoped that experimental studies of this nature will allow the development of guidelines which will enable the landfill operator to dispose of wastes of a hazardous nature with the minimum of disturbance to the environment.

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CHAPTER 1
INTRODUCTION

1.1 INTRODUCTION

The global nature of the increase in the disposal of solid waste (both industrial and municipal) is a cause for concern. In developing countries, these concerns are not any less than in the developed countries; they are possibly magnified, because of their sometimes limited resources. Developing countries are striving for enhanced economic development. An effect of economic development is the greater consumption of energy and resources. An associated adverse effect is the larger production of waste materials. Co-disposal of industrial wastes with municipal wastes is considered by some (Rushbrook, 1990), to be a logical extension of the operation of municipal waste landfilling and probably the easiest and quickest method to bring about an improvement in industrial waste management, especially in developing countries.

The co-disposal of hazardous chemicals with municipal solid waste is practised in South Africa, in suitably constructed containment landfills. However, even with a contained landfill, leachate will be produced and will require treatment, either prior to discharge to the municipal sewerage system, or to a suitable waterway. When co-disposal is practised, it is of importance that the emission of toxic substances from the landfill is not increased to levels that can be detrimental to the surrounding environment. The material of concern in this investigation is a wood preservative commonly called CCA, or Tanalith. The preservative consists of a mixture of copper, chromium and arsenic. The disposal of these substances, both as waste solution and in combination with wood at the end of its lifecycle, has become a matter of concern. The objective of this current study is the development of guidelines for the disposal of CCA within the landfill without any additional degradation of the surrounding environment.

The total production of the various chemicals used for wood preservation is estimated to be excess of 550 000 tonnes per annum (cited by UNEP, 1994). There are three principal preservatives; a waterborne preservative; an organic solvent, and various tar oils, composed of mainly creosote. Copper-chromium-arsenic is classed as a water borne preservative. The global production of chemicals within this class approximates 90 000 tonnes per annum. In South Africa it is estimated that 430 000m^3 of preservative treated wood was produced in 1988.

In the United Kingdom, open burning has been a widely used disposal method for CCA-treated wood utilised for domestic purposes. It has been recommended that wood used in industrial purposes (with a higher proportion of CCA) be incinerated. If these facilities were unavailable the wood should be disposed of to landfill as it was considered the CCA salt was securely bound in the wood (DOE, 1980). There is however, conflicting evidence regarding this viewpoint (Sadler *et al*, 1994). In the USA, the treated wood product is covered by distinctly different regulations than the chemical utilised for wood treatment. In 1992, the EPA published in the Federal register that arsenical-treated wood products

disposed of by the end user are exempt from classification as a hazardous waste, regardless of results from the **T**otal **C**haracteristic **L**eaching **P**rocedure (TCLP) for specified constituents from any individual sample (http://www.awpi.org, 1996). However, the **I**ndustry and **E**nvironmental **P**rogramme **A**ctivity **C**entre (IEPAC) operating under the umbrella of the United Nations is concerned about the disposal of treated timber (UNEP, 1994). It comments that, current disposal options are not encouraging, uncontrolled burning is *out of the question*, incineration of such volumes *impractical*, and disposing to landfill is *not encouraging*.

There is a conflict of opinion with regard to the landfilling of the copper-chromium-arsenic product, as a waste chemical or as the treated wood product at the end of its lifecycle. In developing countries, such as South Africa, with limited resources this problem is magnified. The disposal of copper-chromium-arsenic is worthy of investigation.

1.2 OBJECTIVES

The principal objectives of this investigation were:

The experimental determination of the ability of municipal solid waste to adsorb (and retain) a wood preservative, consisting of a mixture of copper, chromium and arsenic, commonly termed CCA or Tanalith. This material could be disposed of as a waste chemical, or as a treated wood product at the end of its useful lifecycle.

The disposal of this substance should take place with the minimum of environmental risk.

The investigation should consider conditions in South Africa and in particular, conditions existent at the Coastal Park Sanitary Landfill Site, located within the boundaries of the then, Cape Town City Council.

The evaluation of the effect of the co-disposal of the copper-chromium-arsenic wood preservative on biological activities occurring in a landfill in the methanogenic stage of its development.

The evaluation of the effect of the copper-chromium-arsenic on microbial processes was unsuccessful. Deposited municipal solid waste was excavated from Coastal Park Sanitary Landfill Site. It was estimated to have been deposited for approximately one year. It was thought that excavating previously deposited municipal solid waste could be advantageous, as the waste would be partially stabilised and with leachate recycle methanogenic conditions could be rapidly realised. Unfortunately, analysis revealed the period of deposition to have been much longer and the waste was fully stabilised. The emphasis of the investigation was changed to evaluate co-disposal with stabilised municipal solid waste.

1.3 PROCEDURE

The research into the immobilisation of copper, chromium and arsenic in stabilised domestic refuse, comprised of two complementary experimental investigations. A laboratory scale investigation where both kinetic rate constants (adsorption and desorption) and adsorption isotherms were evaluated. A pilot-scale investigation comprising of non-reactive tracer studies, and co-disposal trials. The non-reactive tracer studies allowed the determination of the residence time distribution/deviation from ideal behaviour of the pilot-scale landfill columns. The co-disposal trials conducted at pilot-scale, enabled the evaluation of the kinetic constants together with the residence time distribution trials. It was anticipated that results obtained at pilot-scale could then be up-scaled to be applicable to the full scale landfill.

1.4 ORGANISATION OF THE THESIS

In Chapter 2, a literature survey is presented. The literature review details the composition and disposal routes for municipal, industrial and hazardous wastes with special reference to the differing types of landfilling operations. Waste disposal practices in South Africa are scrutinised. Microbial processes occurring within a landfill are examined, together with the effects of heavy metals on these processes. Heavy metal mobility and attenuation mechanisms in the landfill environment are considered and an analogy is drawn comparing the mobility of heavy metals in soils. Copper, chromium and arsenic are examined as separate entities and in the form of CCA (or Tanalith). The disposal of this chemical is also assessed.

Chapter 3 explores the theoretical considerations of the investigation. Equilibrium and kinetic considerations are probed. Non-ideal reactors and tracer response analysis are detailed. Chapter 4 contains the particulars of the experimental methods and procedures, therein is comprehensive coverage of all the activities undertaken. The results of the investigation together with the associated calculations are shown in Chapter 5.

Chapter 6 discusses relevant aspects of the investigation. The speciation and other physical parameters of copper, chromium and arsenic are catalogued. The adsorption rate and a possible reaction mechanism are postulated. Computional methods are examined, and the effect of co-disposing the metals in an acetogenic, methanogenic and stabilised landfill is given consideration. In Chapter 7 the work undertaken in this investigation is reviewed. Comments are made on the significance of the research and proposals for further work are made.

There are several appendices to the text. Appendix A provides details of the US EPA Toxicity Characteristic Leaching Procedure. Results from the laboratory scale equilibrium and kinetic studies are presented in Appendix B. Pilot-scale results are displayed in Appendices C, D and E. Appendix C provides details of leachate recirculation, while Appendix D shows the results of the residence time trials. Appendix E provides the results of the pilot-scale co-disposal trials. Appendix F refers to further results calculated from the equilibrium studies, Appendix G consists of graphical presentations of the

experimental kinetic data, the modelled fit to these results, together with the associated statistical analysis. Appendix H, I and J reveal the minutiae of the numerical methods and results of calculations, generated from the experimental study. Appendix H contains the calculations associated with the residence time trials. Appendix I reveals the predicted residence time distribution. Appendix J shows the computation to predict chromium concentration in leachate.

CHAPTER 2
LITERATURE REVIEW

2.1 INTRODUCTION

It is a characteristic of all life that it takes suitable raw materials, and converts them into products of value to itself or its species. Unfortunately in doing so it inevitably produces waste material. In the case of modern human life, the intake is of a much wider character and includes fuel, clothes and general commodities (Ministry of Housing and Local Government, 1970). Our waste is correspondingly large and varied, it includes air pollutants, water pollutants and solid wastes. A higher standard of living for the individual means increased consumption of both, materials and energy. This increase in living standards has always been accompanied by a larger volume of more complex residual waste. Industry is not an exception to the above. It uses raw materials, processes them to yield useful products, and is left with waste which is possibly a large percentage of the mass of the raw materials used. It would seem probable, in the foreseeable future, as industry increases in extent and diversity, the waste will also increase in amount and complexity.

A consideration of the Second Law of thermodynamics reinforces previous statements. The Second Law states "No apparatus can operate in such a way that its only affect (in system and surroundings) is to convert heat adsorbed by a system into work" (Smith *et al*, 1975). A direct analogy may be drawn with human beings in virtually any form of their activities. There is not a process that can be operated without the production of waste in some manner or form. An important aspect of the Second Law is the concept of entropy. Entropy may be considered the degree of randomness or disorder in a system. Economists use this facet of the Second Law to illustrate that the recycling of materials cannot eliminate the production of waste (Cairncross, 1993). By implication, the concept of entropy indicates that recycling is inherently inefficient as there is an increasing tendency for entropy, and hence disorder, to increase to a state where nothing of value may be extracted. The logical conclusion is that economic growth cannot be sustained by recycling. Economic growth can only be sustained by the consumption of larger amounts of energy and materials, creating larger amounts of waste.

For more than 5 000 years land disposal of solid residues has been a key element in waste management (Ho *et al*, 1974). Thus, as the population has grown and become progressively more urbanised, a concomitant increase in the number, and size of landfill sites has been necessary. However, pressure to reduce the dependence on landfill as the major option for the disposal of wastes has been gathering momentum in recent years. The most potent driving force for change is the growing opposition from both the public and politicians to landfilling as an environmentally acceptable disposable option (Campbell, 1993). In many of the industrialised countries, environmental legislation was introduced in the latter part of the 1980's and early part of the 1990's. This legislation focused primarily upon the pollution of water and air. This interest is now directed onto the management of solid waste. As greater attention (and legislation) is devoted to aqueous and atmospheric discharges, so industrialists and other producers will dispose of more waste to the land (Cairncross, 1993).

Unfortunately, the present lack of reliable statistics describing the generation, treatment and disposal of waste arisings continues to impair the formulation of appropriate waste management strategies and the assessment of their effectiveness.

2.2 MUNICIPAL WASTES

Municipal wastes typically include household waste, certain white goods and bulky consumer wastes, as well as similar wastes from small commercial and industrial firms, institutions and markets, which are collected and disposed of by, or for, local authorities. There are, however, considerable variations in the exact definition of municipal waste between countries. Due to statistic gathering limitations, especially in developing world regions, the only accurate statement that can be made is that the volume of wastes is rising around the globe. The **O**rganisation of **E**conomic **C**ooperation and **D**evelopment (OECD) estimated that, in 1990 alone, its member countries produced 420 Megatonnes of municipal wastes. Levels of municipal waste also continue to grow on a per capita basis (UNEP, 1993). In the mid-1970's a figure of $1.1 kgday^{-1}$ ($407 kga^{-1}$) was quoted for the OECD; by the end of the 1980's this had risen to $1.4 kgday^{-1}$ ($513 kga^{-1}$). Within the OECD it should be noted that over 90 percent of the population (100 percent of the urban population) has access to municipal collection services. Harris and co-workers (1988) notes that each American produces an average of $2.4 kgday^{-1}$ ($892\ kga^{-1}$).

More than 30 Megatonnes (2.15kg capita per day) of solid waste was generated in the Republic of Korea in 1990 (Lee *et al*, 1993), whilst in 1988, more than 200 Megatonnes of municipal solid waste was generated in the United States (Artiola, 1996). In 1991, the **C**ouncil for **S**cientific and **I**ndustrial **R**esearch (CSIR) undertook a study to evaluate the composition and volume of wastes produced in South Africa (cited by Bredenhann *et al*, 1996). It was estimated that 15 million tonnes of municipal solid waste were being produced per annum. However, this figure excludes the former homeland states, now reinstated within the Republic of South Africa. It is believed, the rate of increase in waste production was in excess of the average annual **G**ross **D**omestic **P**roduct (GDP) of 0.63 percent.

2.2.1 Composition of municipal solid wastes

The composition of municipal wastes varies widely from country to country. Some general trends in the composition of municipal waste can however be recognised. Organic waste accounts for the largest part of municipal wastes. In industrialised countries there appears to be a decline in the percentage of paper and board, with an increase in the plastics content. The proportion of glass and metals have remained stable (UNEP, 1993).

Table 2.1 Composition of municipal solid waste in Developing Countries

Component#	Percent Mass						
	Johannesburg South Africa 1991[a]	Soweto South Africa 1991[a]	Haifa Israel 1979[b]	Agra India 1993[c]	Sao Paulo Brazil 1986[d]	Melbourne Australia 1981[e]	Nairobi Kenya 1994[f]
Paper	34	4	30.3	3.7	28.4	22.9	37.6
Yard	-	-	3.1	10.4	2.3	5.1	1.3
Metal	6	1	3.1	-	4.9	8.3	0.7
Plastics	7	1	4.4	1.4	5.6	3.8	11.4
Food	30	15	54.7	4.3	3.0	41.8	-
Glass	10	2	3.0	0.6	3.1	15.1	-
Other	13	77*	-	79.6	52.7	3.0	49.0

* ash composed 45% of the total analysis

a Chapman & Ekama, 1991 b Raveh & Avnimelech, 1979 c Dayal *et al*, 1993
d Schmidell *et al*, 1986 e Musa & Ho, 1981 f Otieno, 1994

Table 2.2 Composition of municipal solid waste in Industrialised Countries

Component#	Percent Mass				
	Paris France 1992[g]	Berlin FRG 1975[h]	Cincinnati Ohio USA 1982[i]	Typical European household waste 1989[j]	London United Kingdom 1979[k]
Paper	33.0	21.3	50.0	32	37.3
Yard	6.8	-	10.5	-	-
Metal	5.8	6.7	7.8	4	7.2
Plastics	11.7	5.3	8.1	7	3.8
Food	9.7	28.0	1.6	24	23.0
Glass	10.7	13.3	2.8	10	12.0
Other	22.3	25.4	19.2	23	16.7

g Attal *et al*, 1992 h Ehring, 1983 i Rickabaugh *et al*, 1993.
j Rosseaux *et al*, 1989

#The above tables conform to the categories reported by the United States Environmental Protection Agency in 1990 (US EPA, 1990).

South Africa's past political development is indicated by the composition of it's municipal solid waste. The statistics for Johannesburg are similar to that quoted for those in the industrialised countries. Johannesburg was (as defined prior to 1994) predominantly racially categorised as white, its occupants middle class by global standards, their life style being similar to any of the countries being classified as industrialised or first world. Soweto, is the largest "black" township in Africa. The population is almost exclusively African and working class. At the time of this survey (1991) large areas of Soweto were not electrified; this is evident by the low percentage of paper, the absence of any yard (or garden) wastes, and the high percentage of ash. It is probable that these constituents were being utilised as additional fuel for coal burning stoves. The absence of metal and plastic wastes indicates a high degree of scavenging and informal recycling. When considering the composition of municipal waste from Johannesburg the absence of yard wastes is also explainable. Many municipalities in South Africa's wealthier areas collect garden wastes separately.

2.2.2 Disposal routes for Municipal Solid Wastes

Burial in controlled landfills continues to be the most common means of disposing of municipal waste within the boundaries of the OECD. Approximately 70 percent of municipal waste is disposed of in this manner (UNEP, 1993). If one considers the major industrial countries, France disposes of 45 percent of its annual production of municipal solid waste by landfilling (Marticorena *et al*, 1993). The percentage of municipal solid waste landfilled exceeds 75 percent in the United Kingdom, Spain, Canada and the United States. Less than 40 percent of municipal solid waste is landfilled in Switzerland and Sweden, a consequence of the increased importance of incineration in these countries (Little *et al*, 1993). Large landfills in the former Soviet Union cover more than 140 thousand hectares (Nozhevnikova *et al*, 1993); of the 30 Megatonnes of solid waste generated in the Republic of Korea in 1990, 93 percent was landfilled (Lee *et al*, 1993); 200 Megatonnes of municipal solid waste was generated in the United States (Artiola, 1996) in 1988, 73 percent of this material was placed in over 6 000 landfills (Reinhart, 1993). In South Africa, 95 percent of the municipal solid waste generated, is disposed to landfill, only 2.5 percent is recycled, the balance being littered or illegally disposed. It is estimated there are approximately 1 200 municipal waste disposal landfill sites in South Africa (Bredenhann *et al*, 1996).

2.3 INDUSTRIAL AND HAZARDOUS WASTES

Industrial wastes encompass a wide range of substances of varying environmental toxicity. They usually include, general rubbish, packaging, food wastes, acids and alkalis, oils, solvents, resins, paints, and both organic and inorganic sludges. In the OECD area there has been a 50 percent increase in the generation of industrial wastes from 1980 to 1990. In 1990 the mass of industrial wastes generated was estimated at 1.5 Gigatonne per annum (OECD, 1991). A breakdown of disposal operations of hazardous wastes in the European countries of the OECD is shown below (Yakowitz, 1993).

Table 2.3 Ultimate disposal of hazardous wastes within the OECD
(Yakowitz, 1993)

Disposal route	Quantity (Mta^{-1})	As a percentage of the total (%)
Landfill	14-18	70-75
Ocean disposal	0.7	2-5
Incineration	1.5	5-8
Physio-chemical treatment	1.0	4
Recovery	1.5-3.0	5-12

A proportion of the wastes generated by industry are considered to be hazardous wastes as they contain substances that can be toxic to humans, plants or animals, are flammable, corrosive or explosive, or have high chemical reactivity. The OECD has compiled rough estimates of the volumes of industrial and hazardous wastes generated throughout the world. These are summarised below (data refer to the late 1980's) (OECD, 1991). Included in Table 2.4 is data gathered by the CSIR on behalf of the **D**epartment of **E**nvironment **A**ffairs (DEA) in South Africa. The volumes of waste generated are small by global standards but are still considerable, especially in an African context.

Table 2.4 Global Industrial and hazardous waste generation
(OECD, 1991 & DEA*, 1992)

Region	Industrial wastes (Mta^{-1})	Hazardous and special wastes (Mta^{-1})
World	2 100	338
OECD	1 430	303
North America	821	278
Europe	272	24
Pacific	333	
Eastern Europe	520	19
South Africa *	22	2
Rest of the World	158	14

UNEP, as reported by the South African Department of Water Affairs and Forestry (DWAF, 1994b), defines hazardous waste as follows "Waste other than radioactive waste, which is legally defined as hazardous in the state in which it is generated, transported or disposed". The definition is based on chemical reactivity, or toxicity, explosivity or other characteristics which cause or are likely to cause, danger to health or the environment, whether alone or in contact with other waste."

In the United Kingdom the term "hazardous waste" does not have any official meaning. The terms utilised are "notifiable waste" and "special waste" (Cook, 1984). Special waste is defined by the Control of Pollution Act (Special Waste) Regulations. The waste is regarded as special waste if the waste:

* can cause death or serious damage if $5cm^3$ were ingested by a 20kg child
* can cause serious damage to tissue on exposure for less than 15 minutes
* has a flash point of less than 21°C
* prescribed medicinal product

The United States Environmental Protection Agency employs the following criteria to determine whether a waste is hazardous (cited by Cope *et al*, 1983). A waste is hazardous if it is not excluded from other exhaustive listings, and exhibits any of the characteristics of hazardous waste in terms of ignitability, corrosivity, reactivity, or extractive procedure toxicity.

In South Africa, hazardous waste is defined as any waste that directly or indirectly represents a threat to human health, or to the environment, by introducing one or more of the following risks:

explosion or fire;
infections, pathogens, parasites or their vectors;
chemical instability, reactions or corrosion;
acute or chronic toxicity;
cancer, mutation or birth defects;
toxicity, or damage to the ecosystems, or natural resources;
accumulation in biological foodchains, persistence in the environment, or multiple effects.

The South African definition of hazardous waste is based on the UNEP definition stated above (DWAF, 1994b).

The options available for the disposal of hazardous waste in South Africa are; landfill; land treatment; incineration and marine disposal. Incineration is not widely practised in South Africa, there is a lack of facilities, and the high cost of incineration inhibits disposal by that method. Bredenhann *et al* (1996) states there are only approximately 8 incinerators operating in South Africa, all of which are devoted solely to medical waste. Marine disposal in South Africa is declining, in line with international trends, even though it is an inexpensive option. Land treatment is regarded as a pro-active choice of treatment but doubts are expressed in The minimum requirements for the handling and disposal of hazardous waste (1994) whether this method of treatment will attain the necessary environmental criteria. Hazardous waste

may only be disposed at a landfill specifically designed for that purpose. Certain wastes may not be disposed to landfill, while other wastes may only be disposed by landfilling if they are pre-treated before disposal. Wastes that may not be disposed by landfilling are, explosive wastes; waste compressed gasses and radioactive wastes.

2.3.1 Composition of industrial and hazardous wastes

The United Kingdom defines categories of hazardous waste, with further groups and subgroups (Department of the Environment, 1976). It should be noted the data is not comprehensive. Industrial producers add new chemical products at a rate which exceeds one per day and it would be impossible to produce an inclusive definitive list of hazardous wastes (Cope *et al*, 1983).

Table 2.5 Categories of hazardous wastes: I
(adapted from DOE, 1976)

Type of waste	Principle groups
Inorganic acids	All common inorganic acids
Organic acids and related compounds	All acids, acid anhydrides, acid chlorides, etc.
Alkalis	Alkali metal oxides and hydroxides, and proprietary alkaline cleaners
Toxic metal compounds	Cadmium, mercury, lead, arsenic and others.
Non-toxic metal compounds	Iron, etc.
Metals (Elemental)	Alkali, alkaline earth and other hazardous materials.
Metal oxides	Hazardous oxides.
Inorganic compounds	Cyanides, others that liberate toxic gases on acidification, oxidising compounds, toxic compounds, and others.
Other inorganic materials	Asbestos, slag, mineral processing wastes, etc.
Organic compounds	Hydrocarbons including, phenols, peroxides, halogenated compounds, organo-metallics, etc.
Polymeric materials and precursors	Polymeric materials and their associated precursors at all stages of manufacture, rubber, latex, etc.
Fuels, oils and greases	
Fine chemicals and biocides	Pharmaceutical, cosmetics, and biocides.
Miscellaneous chemical waste	Mixed inorganic and organic compounds.
Filter materials, treatment sludge and contaminated rubbish	
Interceptor wastes, tars, paint, dyes and pigments	
Miscellaneous wastes	Tannery and fellmongers wastes, celluloses, etc.
Animal and food wastes	All animal processing wastes.

A similar generalised list of hazardous waste is included in the South African legislation for the handling and disposal of hazardous waste (DWAF, 1994b). A table adapted from the Minimum requirements for the handling and disposal of hazardous waste (1994) is shown below.

Table 2.6 Categories of hazardous wastes: II

(adapted from DWAF, 1994b)

INORGANIC WASTES	OILY WASTES	ORGANIC WASTES
Acids and alkalis Cyanide wastes Heavy metal sludges and solutions Other solid residues	Primarily from the processing, storage and use of mineral oils	Halogenated solvents Non-halogenated solvent residues PCB wastes Paint and resin wastes Biocide wastes
PUTRESCIBLE ORGANIC WASTES	**HIGH VOLUME/LOW HAZARD WASTES**	**MISCELLANEOUS WASTES**
Wastes from the production of edible oils, slaughter house, tanneries and other animal based products	Wastes which based on their intrinsic properties present a relatively low hazard, but may pose problems because of their high volumes	Infectious waste from diseased human/animal tissue Redundant chemicals Laboratory wastes Explosive wastes from manufacturing or redundant munitions

The similarity of the wastes considered hazardous in the South African legislation to that considered hazardous in the United Kingdom is not surprising. South Africa, once a former member of the British Commonwealth, now again, a member, historically based legislation on that current within the United Kingdom.

2.3.2 Disposal routes for industrial and hazardous wastes

It can be seen from Table 2.4, the volumes of wastes being generated are significant. Consider the data below for the disposal of hazardous waste in the United Kingdom (cited by Watson-Craik *et al*, 1992).

Table 2.7 Disposal routes of hazardous wastes in the United Kingdom

Method of disposal	Mass (ta^{-1})	Percentage of the total
Landfilling	1.3×10^6	70
Incineration	9.5×10^4	5
Sea dumping	1.9×10^5	10
Physical or chemical treatment (prior to landfilling)	2.9×10^6	15
Total	1.9×10^6	100

In the United States approximately 80 percent of hazardous waste is currently disposed by landfilling, surface impoundments, waste piles, lagoons, and underground injection wells (Reinhart *et al*, 1991). Referring to the **C**ouncil for **S**cientific and **I**ndustrial **R**esearch (CSIR) study undertaken in 1991 (cited by Bredenhann *et al*, 1996), it was estimated that 1.6 million tonnes of hazardous waste was being generated per annum. Again, this figure excludes the former homeland states within the Republic of South Africa. Of this 1.6 million tonnes per annum, it is estimated that approximately 1 million tonnes are inorganic wastes of which the largest part are cyanide wastes from gold mining. It is suspected that up 50 percent of the non-mining hazardous wastes are illegally disposed of onto municipal solid waste landfill sites, into sewers, or by illegal dumping (Bredenhann *et al*, 1996).

2.4 THE LANDFILL

A landfill may be represented by a simple line diagram. Its inclusion at this point will allow a general description and the introduction of terminology used in the following discussions.

The principal input and output streams to a landfill are shown below in Figure 2.1.

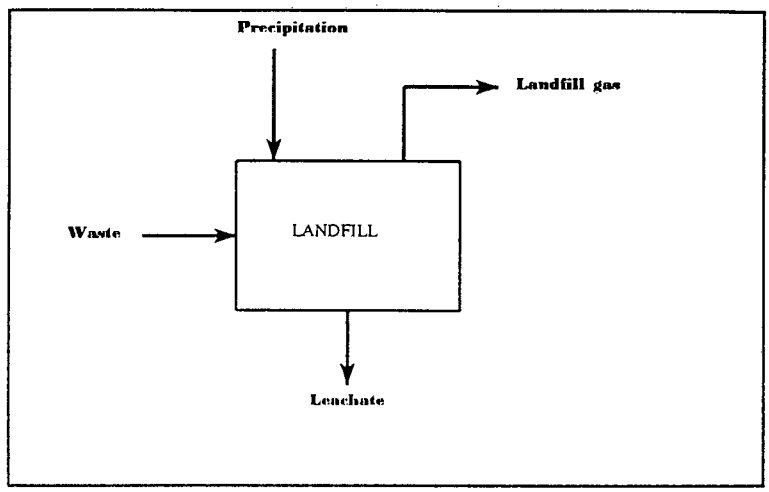

Figure 2.1
Landfills: principal input and output streams

2.4.1 Waste

The majority of wastes disposed of to landfills are solid in nature, although the presence of municipal and industrial sludges is also common. Five major source categories can be identified. These are (Poland *et al*, 1986):

Residential;
Agricultural;
Commercial;
Municipal, and Industrial.

Landfills may be dedicated one specific type of waste (monofill); accept several types of waste (multifill); or may accept a mixture of municipal and industrial wastes (co-disposal) (DOE, 1986). Wastes originating from different source categories will contain different constituents which will also impart different associated characteristics to both the leachate and gas produced. The output streams are briefly discussed below.

2.4.2 Leachate

Precipitation or rainfall may fall onto the landfill. Initially, the solid wastes absorb this additional moisture until such time that field capacity is reached. The field capacity of solid waste is defined as the volume of liquid which can be absorbed by a given weight of solid waste without the release of excess water under the forces of gravity (Harris *et al*, 1988). The infiltration of rainfall into the landfill provides the transport phase for the leaching and migration of contaminants from the landfill. Mechanisms of contaminant removal include the leaching of inherently soluble materials; leaching of soluble biodegradation products of complex organic molecules; leaching of soluble products from chemical reaction, and washout of fines and colloids (Crawford, 1985).

Leachate is highly contaminated water that can emanate from the base of the landfill. It is one of the principal environmental concerns of landfill operation and the escape of leachate into either surface or ground water can significantly degrade their quality. It should be noted that some moisture may be derived from the input wastes; however, the major precursor of leachate formation is infiltration from rainfall.

2.4.3 Landfill gas

Rainfall infiltrating into the landfill is a requirement for biological activity leading to methane production. Upon placement of the municipal solid waste aerobic decomposition will take place. Oxygen, either trapped on placement, or present in moisture, is consumed to produce principally carbon dioxide. After the oxygen is exhausted, anaerobic decomposition is initiated. Initially, carbon dioxide is mainly produced, however as anaerobic decomposition proceeds, methane production is established. The methane concentration of the gas generated from the landfill will eventually reach 50 to 60 percent. A landfill may generate methane at these concentrations for up to 20 years, possibly longer. After the cessation of gas production, anaerobic activity has then ceased and the landfill is said to be stabilised.

2.4.4 Landfill classification

For convenience, from hydrogeological considerations, three categories of landfills may be recognised, although combined characteristics may be often apparent. These are containment sites; attenuation sites and rapid migration sites.

(a) Containment sites

Containment sites are isolated from the environment by the provision of a protracted integrity impermeable or semipermeable barrier of natural or synthetic materials. In Europe, this type of landfill site is often termed "Class I". This type of site is extensively utilised in the former Federal Republic of Germany (Senior, 1990). All hazardous wastes disposed to landfill in South Africa, must be disposed of in a containment site.

(b) Dilute and Disperse or attenuation sites

Protection from groundwater is affected by physicochemical and microbial intervention, commonly termed attenuation. The key requirement is for slow leachate migration through sands and gravel, allowing, hopefully, a significant reduction in the pollutional characteristics of any leachate produced. In Europe, this type of landfill site is often termed "Class II". The majority of landfill sites operating in the United States and the United Kingdom fall within this category (Senior, 1990). Under current South African legislation, with the exception of the very small landfill sites, a dilute and disperse site would be unacceptable.

(c) Rapid migration sites

Rapid migration sites allow little or no environmental protection as leachates can migrate rapidly from the landfill.

2.4.5. Landfill operation

When considering landfill operation one term must be defined at the outset, that of sanitary landfilling. The vast majority of landfills throughout the world are operated in this manner. It was not until the 1930's that the term "sanitary landfill" was introduced. Fresno, California, in a pioneering operation, started compacting solid waste and subsequently covering the compacted waste with soil (American Public Works Association, 1970). The term "sanitary landfill" is appropriate, since the solid waste is disposed in a sanitary manner. The American Society of Civil Engineers (American Society for Civil Engineers, 1976) define sanitary landfilling as "an engineered method of disposing solid waste onto land in a manner that protects the environment, by spreading the waste in thin layers, compacting it to the smallest volume and covering it with compacted soil by the end of each working day, or if necessary, more frequently". In the United Kingdom the term "controlled tipping" is more commonly used than sanitary landfill (Cope *et al*, 1983). In South Africa, landfills are required to be operated in accordance with the principles of sanitary landfilling (DWAF, 1994a).

Landfill operation may be generally classified by the type of waste it receives. As mentioned in Section 2.4.1, landfills may be dedicated to one specific type of waste (monofill). Examples of monofill landfills, are landfills dedicated to accepting power station ash, the disposal of tailings from mining and waste from the bulk production of inorganic chemicals. Multifill landfills accept a limited range of wastes; an example being certain industrial wastes of a similar nature, or mixtures of commercial and industrial wastes. A co-disposal landfill accepts both industrial wastes and municipal solid waste. This study investigates the immobilisation of copper, chromium and arsenic in municipal solid waste. If these materials were disposed of to landfill, usually, this material would be co-disposed. The co-disposal landfill is therefore discussed below in greater detail, than the other landfill operating modes.

(a) Co-disposal landfill and operation

The objectives of co-disposal are to absorb/adsorb, dilute and neutralise any liquids, and to provide a source of biodegradable materials (i.e. municipal solid waste) in order to encourage microbial activity that will assist in the degradation of hazardous compounds (DWAF, 1994b). However, industrial wastes may be present as either a liquid, sludge, solid or dust. For each of these forms of waste the correct method of co-disposal must be decided upon (DOE, 1986). Liquid wastes may be introduced into the landfill by trenching or lagooning; injection or irrigation.

To implement the trenching method, a trench is excavated in the municipal solid waste and liquid waste is then deposited within the trench. The aim of trenching is to provide sufficient interfacial surface area allowing seepage into the waste already deposited. Lagooning is similar to trenching; the difference being, a shallow pit is usually excavated. Injection of liquid wastes is advantageous for wastes with a disagreeable odour. A common method of injection is to build up columns of tyres as the municipal solid waste is placed on the landfill. The liquid waste is then passed down to column and allowed to disperse. Irrigation is practised in the United Kingdom (DOE, 1986), but is not mentioned in the South African requirements possibly a consequence of the danger of spray drift and the health of the landfill staff. Sludges may be disposed of in trenches, or collected at the working face of the landfill, the covered immediately with municipal solid waste. Solids and dusts may be disposed in

a similar manner. South African regulations (DWAF, 1994b) recommend a minimum ratio of one volume of hazardous waste to nine volumes of non-hazardous wastes in order for complete absorption, and to obtain an appropriate dilution of the hazardous waste.

2.5 WASTE DISPOSAL IN SOUTH AFRICA

Waste disposal in South Africa has been thoroughly overhauled in the 1990's. With the publication of Minimum requirements for waste disposal by landfill (1994), waste disposal methods are now comparable with those used in Europe and are stricter and more environmentally acceptable than regulations in countries such as the United Kingdom, where the principles of "dilute and disperse" are still embraced. The particular objectives of the Minimum requirements were the avoidance of degradation of the environment; of the landfill site itself; of the surrounding area; and the implementation of an environmentally acceptable landfilling process (Blight *et al*, 1992).

Historically, waste management in South Africa operated with a minimum of governmental control. Local municipalities such as the City of Cape Town operated landfill sites utilising guidelines initiated in Europe, an example being, the United Kingdom's Department of the Environment's Waste Management series. Until the promulgation of the Environment Conservation Act, No 73, 1989, there was an absence of any effective national control over waste management within South Africa. The promulgation of the aforementioned act did not fully rectify matters. It was not until August 1990 (Sterrenberg, 1996) that the relevant section on waste management was fully implemented. The major effect of the implementation of that section of the Environmental Conservation Act was, in future, landfill sites could only be operated with a permit from central government. The regulations cover the:

registration and licensing of landfill sites;
various impact surveys necessary;
monitoring boreholes, sample frequency and chemical analyses required;
fences, notice boards, etc.;
maintenance of records regarding waste type and volumes;
treatment and/or containment of any leachate produced;
procedure for landfill site closure, etc.

The major requirement from the landfill operator to central government is compliance with the regulations relating to the Minimum requirements for waste disposal by landfill (1994). First published for comment in the Government Gazette in 1985, there have been at least eight updates (Ball *et al*, 1992). The final draft was published in 1994 in three volumes. On publication, it was stated by the relevant minister, the Minister of Water Affairs and Forestry, that the document was open to comment from interested parties for a period of 3 years. The regulations are intended to facilitate conformity with international standards.

2.5.1 Landfill classification

Under the South African system landfills are classified by three means, the; type of waste; size of the waste stream; potential for significant leachate generation.

(a) Waste type

Waste is sorted into two categories; general and hazardous. General waste comprises of what is usually termed municipal solid waste. Waste is considered hazardous if the waste, even in low concentrations, could have a significant effect on public health and/or the environment. The co-disposal of significant quantities of hazardous waste with general waste may only be practised on a hazardous waste landfill.

(b) Size of the waste stream

General waste landfills are classified into four groups: communal; small; medium, and large. This system was adopted to meet the variations that exist in South Africa, and indeed, many developing countries. A small village could not be expected to meet the same requirements or have the same waste disposal needs as a large city. However, hazardous waste landfills are not classified by size, they are classified solely by the hazardous rating of the waste disposed of at that landfill. Any landfill which receives "significant quantities" of hazardous waste must be classified as a hazardous waste landfill.

(c) Leachate generation

The potential for leachate generation is assessed by means of a simplified climatic water balance. It is defined by:

$$B = R - E$$

Where,

B	=	Climatic water balance in mm of water
R	=	Rainfall in mm of water
E	=	Evaporation from the soil surface in mm of water

If the value of B is positive (a worst case *scenario* is employed) the landfill would be classified as having the potential for leachate generation. This unique system was introduced to compensate for the extreme variations of both climatic and socio-economic conditions existing in South Africa. Climatically, South Africa varies from arid desert, to humid rainforest. Socio-economically, conditions vary from those of a typical highly developed industrialised western economy, to those typical of a developing country with corresponding burgeoning population development and its associated poverty and rapid urbanisation (Ball *et al*, 1996).

With the exception of the small communal sites, all landfill sites classified as B+, require leachate management systems. Leachate management may be defined as (DWAF, 1994a) the collection and drainage of leachate to a point where it can be extracted for treatment. This requires a system of drains and a landfill liner. In certain instances, leachate management is synonymous with leachate containment.

Regardless of the climatic water balance, a hazardous waste landfill must be containment or Class I landfill sites. Therefore, all landfills accepting hazardous waste must be separated from the environment by a landfill liner and a leachate collection system.

2.5.2 General waste landfills

General waste is defined in the Minimum requirements as "waste that does not pose an immediate threat to man or the environment, i.e., household waste, builders' rubble, garden waste, dry industrial and commercial waste". As discussed in Section 2.5.1; general waste landfills are classified by the: size of the waste stream; potential for significant leachate generation. The legislative requirements are summarised below. It can be seen that far stricter measures are required at the larger landfill sites than the smaller.

Table 2.8 Requirements of general waste landfill sites in South Africa
(adapted from DWAF, 1994a)

Waste classification	General waste		General waste		General waste		General waste	
Size of waste stream (tonnes day^{-1})	<1		>1 <25		>25 <500		>500	
Landfill classification	Communal		Small		Medium		Large	
Liner requisite	B-	B+	B-	B+	B-	B+	B-	B+
Compacted base layer	None	None	None	Reqd.	Reqd.	Reqd.	Reqd.	Reqd.
Leachate collection layer	None	None	None	Reqd.	None	Reqd.	None	Reqd.
First clay liner	None	None	None	Reqd.	None	None	None	Reqd.
Protecting geofabric	None	None	None	None	None	None	None	Reqd.
Leakage detection layer and underliner	None	None	None	None	None	None	None	Reqd.

2.5.3 Hazardous waste landfills

Hazardous waste is defined in the Minimum requirements as "waste, other than radioactive waste, which is legally defined as hazardous in the state which it is generated, transported, or disposed of." The following types of hazardous waste are specifically mentioned in the Minimum requirements. Inorganic waste; oily waste; organic wastes; putrescible organic

waste; high volume/low hazard waste, which contain small quantities of dispersed hazardous substances.

Hazardous waste landfills are categorised by nature of the hazardous waste received at that landfill. There are two categories of hazardous waste landfill sites in South Africa, they are designated "H:h" and "H:H". Landfills that are engineered to accept all types of hazardous wastes are designated "H:H", while landfills designated "H:h" accept waste that has been evaluated as less hazardous. The engineering criteria of the two different classes of hazardous waste sites is shown below. Subsequently, the determination of the hazardous rating of the waste is addressed, as this determines the class of landfill the waste may be disposed at.

Table 2.9 Engineering requirements of hazardous waste landfill sites in South Africa

(adapted from DWAF, 1994a)

Waste Classification	Hazardous waste (H:h)	Hazardous waste (H:H)
Classification of hazardous waste	Moderate & low hazard waste only Hazard ratings 3 & 4	Extreme, high, moderate and low hazard waste Hazard ratings 1 - 4
Liner requisites		
Compacted base layer	Required	Required
Leachate collection layer	Required	Required
First clay liner	Required	Required
Protecting geofabric	Required	Required
Leakage detection layer and underliner	Required	Required
Second clay liner	Required	Required
Sand cushion layer	None	Required
Flexible membrane liner	None	Required

(a) Determination of the hazardous rating of a waste

Hazardous waste in South Africa is classified in terms of Hazard ratings. The following four sub-categories are employed:

Hazard rating 1: Extreme hazard
Hazard rating 2: High hazard
Hazard rating 3: Moderate hazard
Hazard rating 4: Low hazard

The following criteria must be assessed:

acute mammalian toxicity of compounds in the waste, expressed as LD_{50} ($mgkg^{-1}$);
acute ecotoxicity of compounds in waste, expressed as LC_{50} ($mgkg^{-1}$) of aquatic organisms;
biodegradability (COD or BOD) expressed as a percentage;
accumulation potential, expressed as the octanol/water coefficient, Pow:
persistence potential, expressed as soil adsorption, Koc:
Estimated Environmental Concentration (EEC)

The EEC is the controlling factor. The EEC is calculated from the supposition that the waste is disposed of directly into a body of water, and the risk this action would generate. This is compared with the value of the acute ecotoxicity of compounds in waste, expressed as LC_{50} ($mgkg^{-1}$) multiplied by a safety factor of 10 percent, in order to determine the Hazard rating. The method of calculation is fully addressed in the Minimum requirements for the handling and disposal of hazardous waste (1994).

2.5.4 Waste disposal in South Africa - the current status

The Minimum requirements for waste disposal by landfill has already been adapted for use in Botswana, while other possible applications include Ghana, Tanzania and Uganda. Additionally, the International Solid Waste Association (ISWA) Working Group on Sanitary Landfills, has utilised it as a basis for their document on landfilling in developing countries (Ball *et al*, 1996). This is indicative of the quality of the document and the competence of the researchers and personnel involved in the production of the Minimum requirements .

As stated previously, the documents were introduced in 1994, and are open for comment until 1997. South African response to the document was generally mixed and tended to vary in accordance with the viewpoints of the persons involvement with landfilling. The two main criticisms were either the standards were too high, or the standards were not stringent enough. All comment received was considered. Of relevant comment received, two main categories existed. There was firstly, a misunderstanding of the basic philosophy of the document. Secondly, there were valid ideas which identified areas which required further attention.

The basic philosophy of the document was to utilise a system which was relatively flexible and would be able to be utilised across the broad spectrum of South Africa society, in context with the varying climatic conditions in South Africa. This philosophy is still considered satisfactory. Difficulties were not encountered with the waste classification system; some difficulties were encountered with the size of the operation classification, as the problem of the ultimate size of the landfill was not addressed within the classification system. This was addressed however, in the relevant section on environmental impact. The system to assess leachate generation caused some confusion; it was however, still considered to be acceptable, with some very small minor amendments.

The more important valid ideas to be incorporated into further updated editions of the Minimum requirements included:

prohibition of the landfilling of medical wastes;
public participation, greater emphasis was required;
liner design, to be amended with progress in technology;
scavenging, a problem in developing communities, could not be endorsed but required attention, and appropriate safety measures should be included as an appendix to the Minimum requirements.

Of special interest, within this study, is the issue of co-disposal. A co-disposal minimum ratio of one volume of hazardous waste to nine volumes of non-hazardous waste was initially recommended. Landfill operators were in accord that this ratio was conservative, especially in the drier areas of South Africa. It will now be recommended the site must be trafficable and free of liquid surfaces. The landfill site operator must manage the site in accordance with the climatic water balance. Simply stated, in a wetter climate possibly less liquid may be co-disposed, in a drier climate, more liquid may be co-disposed.

Ball *et al* (1996) concludes that the Minimum requirements for waste disposal by landfill have been successfully implemented and there are not any fatal flaws within the documentation. There is not a requirement for fundamental changes within the document, but the inclusion of worthwhile comment will further improve and augment it. Problems that could possibly arise in the South African context and in other African countries is the implementation of the Minimum requirements. There is a shortage of suitably trained personnel in South Africa and in other African countries. Formulating standards is advantageous only if implementation of those standards is satisfactory.

2.6 THE LANDFILL BIOREACTOR

From a chemical engineering viewpoint, a sanitary landfill is a chemical and biological reactor utilising a heterogeneous feedstock, being partially isolated from the atmosphere and the soil by diffusion gradients which are predetermined by the permeability of the fill material and the adjoining strata (Ellis, 1980). As with any reactor, one must consider the reactions occurring, (in this case, the landfill stabilisation processes in general, and anaerobic digestion in particular) within the reactor, together with the various streams, leachate and landfill gas, exiting from that reactor. Usually, the different modes of reactor operation should also be examined. The following sections examine, initially, the disposal of municipal solid waste, the conventional mode of reactor operation, and subsequently, the effect of co-disposing industrial wastes with municipal solid waste. The co-disposal of copper, chromium and arsenic with municipal solid waste is the principal area of concern in this current work.

2.6.1 Landfill stabilisation processes

After the placement of municipal solid waste within a landfill, a complex sequence of physically, chemically, and biologically-mediated events occur. As a consequence of these events, municipal solid waste is degraded or transformed (Reinhart, 1989). A number of workers have investigated these processes of decomposition, the number of phases of landfill degradation being dependent on the objectives of their investigations. There are two main approaches, the four phase microbially based model developed by Barlaz *et al* (1989), and

the five phase landfill stabilisation model developed primarily by Pohland (Poland *et al*, 1983). Pohland's model correlates events occurring within the landfill with physical changes occurring in the leachate and gas produced by the landfill.

(a) ***Microbially based four phase model***
(adapted from Barlaz *et al*, 1989)

Phase I Aerobic phase
Oxygen is present within the void space when the municipal solid waste is landfilled. Both oxygen and nitrate are present in the moisture associated with this solid waste. Both are consumed with soluble sugars which are the main source of carbon for microbial activity. All the trophic groups required for methanogenesis are present in fresh municipal solid waste (cellulolytics, acetogens, and methanogens), there is however, little change in their populations during this phase.

Phase II Anaerobic acid phase
Carboxylic acids accumulate, there is a corresponding decrease in the pH of the eco-system, with some cellulose and hemicellulose decomposition. The population of the methanonogenic bacteria begins to increase; methane is detected in the landfill gas.

Phase III Accelerated methane production phase
There is a rapid increase in the methane concentration of the landfill gas to values approaching 60 percent. A decrease in carboxylic acid concentrations is evident, together with an increase in system pH. There is little solids hydrolysis, but there are increases in the populations of cellulolytic, acetogenic and methanogenic bacteria.

Phase IV Decelerated methane production phase
Two microbial events occur during this phase. The production of methane, pH and the bacterial populations of both cellulolytic and methanogenic bacteria, remain constant. Within the same time frame, the production of methane decreases, the population of the acetogenic bacteria increases, and carboxylic acids are depleted. There is also an increase in the rate of cellulose and hemicellulose decomposition.

(b) ***Five phase landfill stabilisation model***
(adapted from Poland *et al*, 1983)

Phase I Initial adjustment
Initial waste placement and preliminary moisture accumulates.
Initial subsidence and closure of each landfill area.
Changes in environmental parameters are first detected to reflect the onset of stabilisation processes which are trending in a logical fashion.

Phase II Transition
Liquid is present in excess of field capacity and leachate is formed.
A transition from initial aerobic to anaerobic microbial stabilisation occurs.
The primary electron acceptor shifts from oxygen to nitrates and sulphates with the displacement of oxygen by carbon dioxide in the gas.
A trend toward reducing conditions is established.

Measurable intermediates such as volatile organic fatty acids first appear in the leachate.

Phase III Acid formation

Intermediary volatile organic fatty acids become predominant with the continuing hydrolysis and fermentation of waste and leachate constituents.
A precipitous decrease in pH occurs with a concomitant mobilisation and possible complexation of metal species.
Nutrients such as nitrogen and phosphorous are released and utilised in support of the growth of biomass commensurate with the prevailing substrate conversion rates.
Hydrogen may be detected and this will affect the nature and type of intermediary products formed.

Phase IV Methane fermentation

Intermediary products appearing during the acid formation phases are converted to methane and excess carbon dioxide.
The pH returns from that controlled by the volatile organic fatty acids to one characteristic of the bicarbonate buffering system.
Oxidation-reduction potentials are at their lowest levels.
Nutrients continue to be consumed.
Complexation and precipitation of metals species proceed.
Leachate organic strength is dramatically decreased in correspondence with increases in gas production.

Phase V Final maturation

Relative dormancy following active biological stabilisation of the readily available organic constituents in the waste and leachate.
Nutrients may become limiting.
Measurable gas production all but ceases.
Natural environmental conditions become reinstated.
Oxygen and oxidised species may slowly reappear with a corresponding increase in oxidation reduction potential.
More microbially resistant organic materials may be slowly converted with the possible production of humic-like substances capable of complexing with, and re-mobilising heavy metals.

2.6.2 Anaerobic biological processes

(adapted from Speece, 1983)

The bioconversion of organic material to methane is accomplished by a consortium of bacteria comprised of chemoheterotrophic, nonmethanogenic bacteria and methanogenic bacteria. Complex organics are first hydrolysed by the chemoheterotrophic nonmethanogens to free sugars, alcohols, volatile acids, hydrogen and carbon dioxide. Subsequently, the alcohols and volatile acids longer than two carbons are oxidised to acetate and hydrogen by obligate proton reducing organisms called acetogens, which must exist in a symbiotic relationship with hydrogen utilising methanogens.

In the final step, acetate and hydrogen are converted to methane by methanogenic bacteria. Acetate is the most important substrate for methanogens. Jeris *et al* (1965) conducted a series of experiments with a batch operated laboratory sewage sludge digester, in which they showed that acetic acid is the most prevalent volatile acid intermediate formed in the fermentation of fats, carbohydrates and proteins. Approximately 70 percent of the methane produced, results from the degradation of acetic acid.

An obligate, syntropic relationship exists between the acetogens, which convert the higher volatile acids to acetate and hydrogen, and the hydrogen-utilising methanogens. Hydrogen partial pressure must be maintained at an extremely low level, to enable favourable thermodynamic conditions for the conversion of volatile acids and alcohols to acetate. Under standard conditions of one atmosphere of hydrogen, the free energy change is positive for this conversion and thus precludes this reaction. An example of this is the conversion of propionate to acetate and hydrogen. The free energy does not become negative until the hydrogen partial pressure decreases below $10^{-9}Nm^{-2}$. It is therefore obligatory that the hydrogen utilising methanogens maintain these extremely low hydrogen partial pressures in the system; otherwise, the higher volatile acids, such as propionic and butyric will accumulate in the system. Fortunately, the hydrogen utilising methanogens in this physiological partnership are adept at this and normally perform this service with ease, to permit the reaction to proceed efficiently to full methane production.

The major groupings of bacteria and the reactions they mediate, are as follows:

1: fermentative bacteria,
2: hydrogen-producing acetogenic bacteria,
3: hydrogen-consuming acetogenic bacteria,
4: carbon dioxide-reducing methanogens,
5: aceticlastic methanogens.

The metabolic steps and microbial groups involved in anaerobic digestion are shown below.

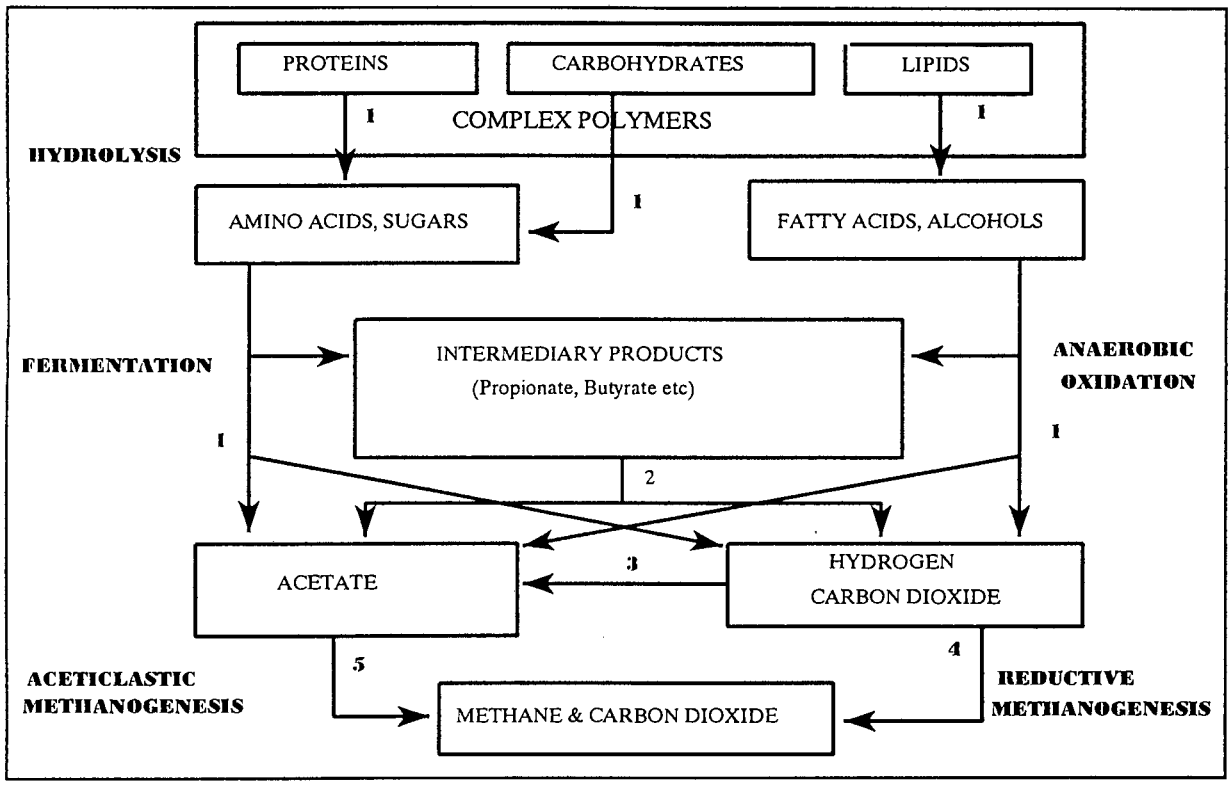

Figure 2.2
Reaction scheme for the anaerobic digestion of polymeric materials
(cited by Pavlostathis *et al*, 1991)

The nature and chemical composition of the materials used in anaerobic digestion dictate those degradation sub-processes which are operative, and the microbial groups involved in these processes. The table below (Table 2.10) shows the composition of primary and activated sludge, common substrates for anaerobic digestion, with the inclusion of the composition of municipal solid waste for comparison. It can be seen from the table that the substrates are similar in nature, with only the cellulose content and protein content being significantly different. The major component of activated sludge is crude protein. Primary sludge has a relatively high lipids content. The principle substrates which decompose in landfills to form methane are cellulose and hemicellulose (Barlaz *et al*, 1989). The bioconversion of biopolymers (principally cellulose, hemicellulose, and protein) is accomplished by three trophic groups of anaerobic bacteria. These are:

hydrolytic and fermentative bacteria,
acetogenic bacteria,
methanogenic bacteria.

Barlaz *et al* (1989) found all these trophic groups present in fresh municipal solid waste.

Table 2.10 Composition of primary sludge, activated sludge, and municipal solid waste

Component	Primary Municipal Sludge (Higgins *et al*, 1982)	Activated Sludge (US EPA, 1979)	Municipal Solid Waste (Barlaz, 1988)
Volatile solids	75.0	59-75	78.6
Lipids	10.3	5-12	-
Cellulose	32.2	7	51.2
Hemicellulose	2.5	-	14.9
Lignin	13.6	-	15.2
Crude protein	19.0	32-41	4.2
Volatile acids	6.4	-	-
Ash	25.0	25-41	21.4

2.7 THE LANDFILL BIOREACTOR - THE ASSOCIATED ENVIRONMENTAL HAZARDS

There is a need for the sound environmental management of every aspect of landfill activities in order to minimise, and whenever possible, eliminate, any adverse effects. These effects range from visual intrusion to more easily measurable impacts such as leachate and gas migration. Campbell (1993) was concerned with the following:

Leachate;
Gas;
Site Restoration;
General matters, including vermin, flies, birds, litter, dust, smell, mud on roads, visual intrusion, noise and traffic.

2.7.1 Leachate

Before 1965 very few people were aware of the fact that water passing through municipal solid waste in a landfill would become highly contaminated (Boyle *et al*, 1974). This water, termed leachate, was generally not a matter for concern because only a few causes had been noted where leachate was detrimental to the environment. Leachate from a landfill site containing biodegradable matter, such as municipal solid waste, may be defined (Harris *et al*, 1988) as a complex organic liquid, formed primarily by the percolation of precipitation water through the open landfill, or through the cap of the completed fill. The resulting leachate is a complex and highly variable mixture of soluble organic, inorganic and bacteriological

constituents and suspended solids in an aqueous medium. The exact composition is variable and site specific. Many workers have analysed leachates and details of their analyses abound in the literature (Robinson, 1980; Iza *et al*, 1992; Kennedy *et al*, 1988; Mott *et al*, 1987). Robinson *et al* (1982) cites the results of a survey undertaken by himself in 1979. He and his co-workers sampled 15 landfill sites in the United Kingdom. The results are summarised below in Table 2.11. The results show the composition of leachates and emphasize the wide range of concentrations of the constituents.

Table 2.11 Composition of leachates from municipal solid waste landfills, ranges of concentrations in samples

(adapted from data cited by Robinson *et al* , 1982)

Determinand	Range	Determinand	Range
pH value	6.2-7.4	Mg	12-480
COD	66-11600	K	20-650
BOD	<2-8000	Ca	165-1 150
TOC	21-4400	Cr	<0.05-0.14
Amm.-N	5-730	Mn	0.32-26.5
Org.-N	ND-155	Fe	0.09-380
Nitrate-N	<0.5-4.9	Ni	<0.05-0.16
Nitrite-N	<0.2-1.8	Cu	<0.01-0.15
Ortho-P	<0.02-3.4	Zn	<0.05-0.95
Chloride	70-2777	Cd	<0.005-0.01
Sulphate	55-456	Pb	<0.05-0.22
Na	43-2500		

(All results, except pH, are expressed in $mg\ell^{-1}$)

As far back as 1982, groundwater contamination had become one of the United States most pressing environmental problems (Evans *et al*, 1982). The earliest documented case of groundwater pollution from impounded garbage was reported by Calvert in 1932 (Calvert, 1932). Calvert reported increased levels of calcium, magnesium, chlorides, total organic nitrogen, total solids and carbon dioxide in a well more than 150m from the impounding pit. Since this historic reference there have been many reported incidences where leachate has contaminated the surrounding soil and polluted an underlying groundwater aquifer or nearby surface water (Chain *et al*, 1976; Reinhard *et al*, 1984; Albaiges *et al*, 1986; Assmuth *et al*, 1993).

2.7.2 Landfill gas

Landfill gas is a mixture of gases produced by microbiological activity on putrescible/biodegradable or other similar material deposited in a landfill site. When large amounts of solid waste accumulate, the landfill site acts as a bioreactor in which micro-organisms produce a biogas typically composed of approximately 35-40 percent carbon dioxide and 60-65 per cent methane (Freestone *et al*, 1994). In addition to the major components, landfill gas contains an extremely wide variety of components in trace amounts (DOE, 1986; Poland *et al*, 1986b). These components are too numerous to tabulate. A summary of these trace components contained in landfill gas is shown below in Table 2.12.

Table 2.12 Landfill gas composition
(adapted from DOE, 1986)

Component	Typical value (mature refuse) [%volume]	Component	Typical value (mature refuse) [%volume]
Methane	63.8	Unsaturated hydrocarbons	0.009
Carbon dioxide	33.6	Halogenated compounds	0.00002
Oxygen	0.16	Hydrogen sulphide	0.00002
Nitrogen	2.4	Organosulphur compounds	<0.00001
Hydrogen	<0.05	Alcohols	<0.00001
Carbon monoxide	<0.001	Others (not included above)	0.00005
Saturated hydrocarbons	0.005		

There have been many cases reported where methane produced in domestic landfills has migrated into adjacent properties. Explosive concentrations have accumulated and caused an explosion. The consequences have been property damage, personal injury and even loss of life. Such problems received little attention until the early 1970's (DOE, 1990). Even then, early efforts to evaluate gaseous emissions from landfills were primarily concerned with methane and the associated dangers of explosions, fires, and potential asphyxiation of surrounding residents in their homes. As studies in landfills increased in numbers and the level of technology improved, many incidents of the generation of toxic organic compounds were reported. The State of California has enacted a law to compel landfill owners to monitor for 26 volatile organic compounds (Rickabaugh *et al*, 1993).

Gas production in landfills is affected by many variables, Pohland reviewed a number of sources and considered the major variables on gas production (Poland *et al*, 1986b) to be, the:

nature of the solid waste;
moisture content;
particle size and degree of compaction;
buffer capacity;
nutrients;
temperature;
method of gas extraction.

2.8 CO-DISPOSAL OF INDUSTRIAL WASTES WITH MUNICIPAL SOLID WASTES

The co-disposal of industrial wastes with municipal solid waste is regarded by some researchers, such as Rushbrook (1990), as a logical extension of the operation of municipal waste landfilling. Rushbrook considers that co-disposal is probably the easiest and quickest method to bring about an improvement in industrial waste management, especially in developing countries.

Since the early 1970's scientific research has examined the environmental aspects of co-disposal (DOE, 1975). A limited programme of research was started in March 1972 by the then, Water Pollution Research Laboratory. They examined 19 landfill sites, situated in various geological formations and accepting a wide range of hazardous wastes. Full scale studies were supported by further work at pilot and laboratory scale (Bromley *et al*, 1981). Co-disposal is widespread in the United Kingdom (Little *et al*, 1993) and is institutionally supported by the Department of Environment and the Harwell Laboratory, a prestigious institution that has principally been involved with nuclear development (Arnott, 1985). The text of the latest proposed **E**conomic **C**ommunity (EC) Landfill Directive, if implemented, will prohibit the establishment of new co-disposal landfill sites. However, in the United Kingdom, the existing capacity of current sites means, in principle, that co-disposal would continue for many years (DETR, 1996), and documentation supplied by the **D**epartment of the **E**nvironment, **T**ransport and the **R**egions is still supportive of co-disposal (DETR, 1996).

In the United States, before the passage of the **R**esource **C**onservation and **R**ecovery **A**ct (RCRA) in 1976, there was very little control in many areas over the landfilling of industrial wastes (Lee *et al*, 1984). The co-disposal of industrial wastes with municipal solid wastes did not violate any regulatory laws, and Graham (1985) estimates that thousands of municipalities in the United States accepted industrial wastes in their landfills as a service to local industries. Currently, in the United States (Little *et al*, 1993) there is not any federal legislation which expressly forbids the co-disposal of municipal and other waste, provided that the appropriate treatment and landfill engineering standards are met. If the waste disposed with municipal solid waste, is classified as hazardous waste, then disposal standards for hazardous waste have to be met. There is thus an economic incentive not to dispose hazardous waste with municipal waste, and therefore co-disposal of such waste is not widely practised. In Denmark, municipal solid waste and industrial waste is separated into two

distinct streams (Arnott, 1985). Co-disposal is practised in South Africa and is encouraged within the Minimum requirements documentation. A minimum ratio of one volume of hazardous waste to nine volumes of non-hazardous waste is recommended. This should allow sufficient dilution of the hazardous waste and allow the provision of sufficient absorptive capacity.

Co-disposal may be defined as the conscious deposition of hazardous wastes with household or similar wastes to obtain specified objectives, a key element of which is to take advantage of attenuation processes inherent within the landfill site (DOE, 1986). Co-disposal utilises those properties available in the municipal solid waste, to attenuate the constituents present in the hazardous waste, that could be detrimental to the environment. These attenuation mechanisms have been conveniently summarised (DOE, 1986).

Attenuation processes

Physical Absorption, adsorption, filtration, dilution and dispersion.

Chemical Acid-base interactions, oxidation, reduction, precipitation, co-precipitation, ion-exchange and ion formation.

Biological Aerobic and anaerobic microbial degradation.

The effective co-disposal of substances which are inherently non-biodegradable (such as heavy metals), is dependent upon dilution to reach environmentally acceptable standards or immobilisation within the landfill (Watson-Craik, 1987). The concept of dilution is addressed in Section 2.8.1.2.

When one considers the above attenuating mechanisms, it is also valuable to consider factors which could enhance the mobility of metal ions within the landfill environment. One example is the lowering of pH, an instance being a landfill within the acetogenic phase of activity. Other factors worthy of consideration are, redox changes, inorganic and organic complexation and microbially mediated species transformations such as biomethylation (Forstner *et al*, 1995).

2.8.1 Physical attenuation mechanisms

2.8.1.1 Absorption

When considering the mechanism of absorption within the landfill environment, a critical requirement is the thorough understanding of the landfill site water balance. The water balance or water budget technique is an application of the conservation of mass and continuity of flow of liquid to and from the landfill (Blight *et al*, 1992). Unfortunately, the task of determining the water balance for a particular site is not a simple matter. The interrelationships between climate, vegetation, soil characteristics, and their effect on run-off, evapotranspiration and vertical drainage are complex (Peyton *et al*, 1988). To obtain

maximum absorption of co-disposed industrial wastes, it is necessary to avoid any additional inputs of moisture such as groundwater infiltration. Additional factors to consider could include:

the rate of placement of the municipal solid wastes;
the rate and placement of any liquid waste;
moisture generated by metabolic activity;
moisture content of fresh solid waste;
composition of the emplaced municipal solid waste.

The infiltration of moisture into the landfill and its absorption by the solid waste can delay the formation of leachate. The are two predominant mechanisms for the retention of moisture in solid waste (DOE, 1986). Liquid may be absorbed into the waste and retained by capillary attraction within the microparticles of the solid waste. Liquid may also fill and be subsequently retained by voidage volume formed upon the placement of the solid waste at the landfill site. The degree of compaction of the solid waste has a significant effect on the magnitude of water retention displayed by the solid waste. At higher compaction densities absorptive capacity falls sharply. At compaction densities of 700-800kgm^{-3} it is estimated the solid waste could absorb 0.1-0.2m^3 of added moisture per cubic metre of solid waste. When compaction densities are achieved, absorptive capacities may be reduced to as little as 0.02-0.03m^3 of moisture per cubic metre of solid waste (DOE, 1986).

2.8.1.2 Dilution and dispersion

The United Kingdom's Department of the Environment are strong proponents of the principle of the "dilute and disperse" approach to waste disposal. At low concentrations, wastes which at greater concentrations could be extremely hazardous, can be safely disposed at landfill sites. Dilution and dispersion can occur naturally where these materials are randomly distributed in the waste. In other cases, dilution can be achieved by spreading a consignment of the waste in question along the landfill working face. As more waste is then received, the compaction of that waste with waste previously received, the material would be "diluted and dispersed" within the landfill.

There is another aspect of the policy of dilution and dispersion to be considered. There is not only the dilution and dispersion of hazardous materials within the landfill, but dilution and dispersion into the surrounding environment. To illustrate the principle of dilution and dispersion consider the disposal of solid cyanide waste (DOE, 1976). Levels of cyanide that can be deposited are, 1 000gm^{-3}, at a Class I (Section 2.4.4(a)), or containment site, 10gm^{-3} at a Class II (Section 2.4.4(b)), or attenuation site and 1gm^{-3} at a Class III (Section 2.4.4(c)) or rapid dispersion site. A further limitation is that for a Class I site, the landfill must be limited to a cyanide content of 10gm^{-3} averaged over 1 000m^3, for a Class II site the cyanide content would be limited to 1gm^{-3} again averaged over 1 000m^3. This figure is justified by the British authorities, as surveys of municipal solid waste in the United Kingdom have found that trace levels of cyanide approximate 1gm^{-3}. Further justification is outlined by the example included in the document (DOE, 1976). Considered is a landfill site receiving a volume of municipal solid waste approximating 100m x 100m x 2m per annum, the average

cyanide concentration being $1gm^{-3}$. It is assumed that all the cyanide deposited within the landfill is leached at the same rate it is deposited, and passes directly into a large water body flowing at 45 $000m^3day^{-1}$. Then,

Mass of cyanide deposited per annum
= 100 x 100 x 2 x 1 = 20 000g

Volume of water passing under landfill per annum
= 4 500 x 365 = $1.6425 \times 10^6 m^3$

Concentration of cyanide would be elevated
= $20000/1.6425 \times 10^6$ = $0.01mg\ell^{-1}$

The approach outlined above appears reasonable and uncomplicated to control. However, the variety and toxicity of wastes being co-disposed should not be underestimated. Cheyney (1984) tabulates wastes deposited in one section of the Stewartby landfill site in Bedford, United Kingdom, during the period 1978-1980. The wastes are to numerous to catalogue here; to indicate the extent of the wastes mentioned, examples are, 579 tonnes of phosphoric acid, 2121 tonnes of biocide, 220 tonnes of toxic metals, 8300 tonnes of adhesive wastes, 1707 tonnes of mixed organic compounds, and 2908 tonnes of tannery wastes.

2.8.1.3 Adsorption

Adsorption is a process where, usually, molecules within a fluid phase become attached to a solid phase. However, the adsorbent surface may be an interface between gas and liquid, liquid and liquid, or liquid and solid. The process is usually selective in all practical applications, where one component within a multi-component mixture is preferentially adsorbed to a greater extent. Two types of adsorption may occur (Smith, 1981):

(a) Physical adsorption

Physical adsorption is non specific and the forces holding the fluid molecules to the solid phase are relatively weak. The bond between the phase consists of van der Vaals' energy, dipole-dipole interactions or electrostatic energy, as in the case of hydrogen bonding. The heat of physical adsorption is usually in the range, 2-15kcal $gmol^{-1}$, the larger values occurring in hydrogen bonding or in the cases of multiple point contact (Graham, 1959). Equilibrium between the solid surface and the solute molecules is usually rapidly achieved and readily reversible.

(b) Chemical adsorption (chemisorption)

Chemisorption is specific and involves forces greater than physical adsorption. The form of molecular bonding in chemisorption may be considered as a chemical bond, which is often irreversible. The heat of adsorption is usually in the range of 30-100kcal $gmol^{-1}$. Chemisorption differs from an ordinary chemical reaction in the fact the reacting atoms of the solid surface retain their identity with the original lattice (Graham, 1959). Chemisorption is usually preceded by physical adsorption, the chemical bond being formed only after the

necessary activation has been provided. The major criteria for effective adsorption is intimate contact of the solution with the solid adsorbent, thereby permitting the mass transfer of the solute ions to the adsorbent (Malina Jnr., 1967). An important characteristic of chemisorption is that the magnitude of adsorption will not exceed that corresponding to a monomolecular layer (Smith, 1981). This limitation occurs because the valence forces causing the molecule to adhere to the surface decrease rapidly with distance.

(c) Adsorption of heavy metals onto municipal solid waste

The extent and reversibility of adsorption of any material onto municipal solid waste is dependent on a number of factors. These include:

the chemical form of the metallic waste;
the available surface area for adsorption;
the pH of the municipal solid waste;
the character of the available surface area;

Watson-Craik (1990) examined factors influencing the adsorption of inorganic wastes, (such as heavy metals) onto municipal wastes. She admits there is a paucity of available data, and reviews two studies. Both studies examine the adsorption of arsenic onto municipal solid waste. The research methods employed by the two researchers are different, and Watson-Craik thought their conclusions, when compared, to be conflicting. The results of the two studies are shown overleaf in Table 2.13.

One of the studies Watson-Craik evaluated was presented by Blakey (1984) of the United Kingdom's Water Research Centre, Landfills Section. It is likely this work played a significant part in the development of the current practices in co-disposal in the United Kingdom and is therefore worthy of closer consideration. Blakey evaluated the adsorption of arsenic(III) onto municipal solid waste in the concentration range 1.25mgℓ^{-1} - 100mgℓ^{-1}, and arsenic(V) in the range 2.5mgℓ^{-1} - 200mgℓ^{-1}. The municipal solid waste was only categorised as *fresh* and *aged* ; the waste was not categorised further. The pH range of the investigation was 5 to 9; the investigation was executed at laboratory scale.

Adsorption tests were completed using distilled water as the aqueous carrier, desorption tests were conducted with landfill leachate as the aqueous carrier. Adsorption equilibrium was generally reached, in all cases, in less than 24 hours, the results conformed to a conventional Freundlich isotherm. In general, an increase in pH increased the adsorption of arsenic(III), which was greatest in aged solid waste. The amount of arsenic(V) adsorbed reached a maximum at pH 7, with little difference of the adsorption characteristics of the new and aged solid waste.

The principal differences between the studies conducted by Jones and co-workers (1978) and that conducted by Blakey (1984) were:

(i) Blakey employed authentic solid waste, while Jones's solid waste was artificially assembled.
(ii) Blakey utilised anaerobic conditions, while Jones utilised aerobic conditions.
(iii) Blakey used distilled water as the liquid medium, Jones used a 82mM solution of acetic acid.

Table 2.13 Adsorption of arsenic onto municipal solid waste

(adapted from Watson-Craik, 1990)

	Study	
	(Blakey, 1984)	(Jones *et al*, 1978)
Substrate	1kg of pulverised municipal solid waste	10g of artificially assembled solid waste
Test conditions	Anaerobic, at a temperature of 25°C	Aerobic, at a temperature of 30°C
Arsenic concentration range ($mg\ell^{-1}$)	1.25 - 100 [arsenic(III)] 2.5 - 200 [arsenic(V)]	18 - 190 [arsenic(V)]
Isotherm derived	Freundlich	Langmuir
Dependency of adsorption on pH (pH5 to pH9)	Arsenic(III): Adsorption increased with pH Arsenic(V): Adsorption maxima at pH7	Arsenic(V): adsorption decreased with pH
Desorption	Arsenic(V): Desorption was less than 5 percent of that adsorbed from aged refuse, the pH range being 5 to 7.	Arsenic(V): Partial or complete desorption, the pH range being 7 to 9.

There would not appear to be any point of agreement in the results presented by the two researchers. This illustrates the difficulty of interpreting and subsequently implementing, research results by a practitioner of co-disposal of industrial wastes with municipal solid waste. The absence of standardised procedures for examining the adsorption characteristics coupled with the heterogeneous nature of solid waste received at landfill sites, will possibly contribute conflicting information.

(d) Adsorption of heavy metals onto soils

The adsorption of the various heavy metals onto soils is well documented. It is of great interest to examine factors which could be applicable to the landfill environment. Soil is a heterogeneous porous medium, normally consisting of about 95 percent inorganic material and 5 percent organic material. The inorganic material is primarily composed of sand, silt and clay. Organic matter present is primarily composed of plant residues, the principal constituents being cellulose (15-60 percent dry weight), hemicellulose (10-30 percent dry weight) and lignin (2-30 percent dry weight). The pH of soil can vary from less than 5.5 to greater than 8.5. Areas of high rainfall, usually have higher levels of organic matter and

hence tend to be acidic in nature. The oxygen content of soils is dependent on soil moisture content. In soils saturated with water, the soil oxygen content is very low (Pepper, 1996).

The similarities with municipal solid waste in the landfill environment are evident. Both are heterogeneous porous materials, existing in a similar pH range. Both anaerobic and aerobic conditions can exist in both soils and solid waste. The organic matter present, and its composition in soil, is similar to that present in solid waste (see Table 2.21). Additionally, soil is employed on the landfill as cover material and is compacted into the solid waste as successive layers of solid waste are deposited. The above, together with the paucity of data concerning the adsorption characteristics of solid waste, make examination of the behaviour of heavy metals in the soils medium, relevant to this study.

Many researchers have examined various aspects of the behaviour of arsenic(III) and arsenic(V) in soils. The ranges of Eh and pH in soils can lead to either As(V) or As(III). Microbial activity can cause methylation, demethylation and/or a change in oxidation state (O'Neill, 1990). Under strongly reduced environments, elemental arsenic and arsenic hydride (AsH_3) can exist. Under moderately reduced conditions, arsenic(III) dominates; arsenic(V) is the stable form in an oxygenated system (Deuel *et al*, 1972; Hess *et al*, 1976). This is of great importance in the landfill environment where anaerobic conditions, and hence reducing conditions, exist (Gould *et al*, 1989). A survey conducted in the Tamar Valley, South West England, showed; in aerobic soils, 90 percent of the arsenic present was in the form of As(V) (arsenate); in anaerobic waterlogged soils As(V) was present 15 to 40 percent (O'Neill, 1990). Ferguson and Gavis (1972), in their review of the arsenic cycle in natural waters, state that at the high Eh values encountered in oxygenated waters, arsenic acid (As(V)) species (H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}) are stable. At Eh values characteristic of mildly reducing conditions, arsenous acid (As(III)) species (H_3AsO_3; H_2AsO_3- and $HAsO_3^{2-}$) become stable. This indicates that arsenic added to an anaerobic landfill in the form of arsenic(V) would be fully reduced in time to form arsenic(III). Therefore, in the following review the behaviour of arsenic(III) and arsenic(V) will be examined.

Korte and co-workers (1976) investigated the relative mobilities of eleven trace elements in laboratory scale soil columns. The researchers objective was to determine which soil properties (physical and chemical) control the movement of the trace elements. Amongst the metals examined were copper(II), chromium(III) and arsenic(III), which are of specific interest to this current study. Copper was in the form of chloride, while both chromium and arsenic were in the form of their oxides. Of interest to this particular study; the aqueous carrier selected for the experimental procedure was municipal solid waste leachate. The initial concentration of metals in solution varied from 70 to 120mgℓ^{-1}. Unfortunately, the initial pH of the leachate was adjusted to 3 to prevent the precipitation of lead, one of the metals under examination. The pH of leachate, from a methanogenic landfill, is usually in the range 6.2 to 7.4. The researchers reported that copper was immobile in all the soils except one, a sandy Wagram soil. It's mobility was however, also low in that soil. The researchers also reported the behaviour of copper could not be correlated with soil properties. Arsenic and chromium exhibited similar behaviour to one another; they were on average more mobile than other metals evaluated. The other metals included lead(II), and nickel(II) both relatively common constituents in landfill leachate. The researchers were unable to correlate soil chemical and physical properties with cation mobility even though detailed statistical analysis of the results was practised.

Elfving and co-researchers (1994) examined the mobility of arsenic and lead in old orchard soils in Ontario. Lead arsenate had been used for insect control for many years in the locality. The researchers confirmed the work of others, showing that arsenic(V) has a low mobility in soils; arsenic concentration in soil decreasing relatively sharply with depth. The researchers did not comment further on arsenic mobility. Sadler and others (1993) investigated soil and water contamination at a former tannery in Brisbane, Australia. The former tannery land is now the site of a school, the Craigslea State School. The researchers were surprised at the degree of arsenic contamination with depth, and mention previous studies that indicated a fairly limited arsenic mobility in soils. However, arsenic was used extensively in the form of sodium arsenite (arsenic(III)) at the former tannery, and cite a study where sodium arsenite was shown to be fairly mobile in sandy soils. During the same investigation, laboratory leach tests were carried out with distilled water. Arsenic leached from the contaminated soils in all cases. Some soils leached arsenic in significant quantities; a soil concentration of 190mgkg^{-1} resulted in a leachate concentration of 47$\mu g\ell^{-1}$. Sadler concluded that arsenic mobility in soils was affected by the species of arsenic present, together with the nature of the soil; arsenic(III) was more mobile than arsenic(V); the transformation from one to the other being influenced by the redox potential and the prevailing pH value.

The adsorption of arsenic onto the organic component of soils was examined by Thanabalasingam and Pickering in 1986 (cited by O'Neill, 1990). The maximum sorption of arsenic(V) by humics occurred at pH5.5 with the arsenic(III) maxima occurring at higher pH values. In general, the humics sorbed 20 percent less arsenic(III) than arsenic(V) and the sorption behaviour could be described by a Langmuir-type isotherm, with some deviation at higher concentrations. It appeared the humics were acting as anion exchangers as the pH values became more alkaline the humics became more soluble, and their ability to remove arsenic from solution was reduced (O'Neill, 1990). Unfortunately, the term "more alkaline" was not defined further. However, pH5.5 is near that of landfill leachate and one would expect some degree of adsorption of arsenical compounds, especially arsenic(V).

Elkhatib and co-researchers (1984) investigated the sorption and desorption of arsenite (arsenic(III)) onto five West Virginian soils. The liquid carrier employed in the investigation was de-ionised water. The Freundlich equation described sorption from an initial concentration of 5 to 1 000mgℓ^{-1}. The rate of sorption was initially rapid, but decreased with time. From all starting concentrations, initial sorption was rapid, 80 percent of the maximum sorption was achieved within the first 30 minutes; subsequent to that, sorption rates levelled out. The initial rapid sorption suggested a high energy sorption associated with low surface saturation. The slow reaction was assumed to be a result of increased surface negative charge and decreased sorption energy (Kuo *et al*, 1974). Desorption experiments indicated that arsenic(III) was irreversibly sorbed by the soils examined, only a small fraction of the arsenic(III) being desorbed from the soils. A modified Freundlich equation described the rate of arsenic(III) adsorption and desorption. The pH of the deionised water-soil mixture varied from 4.20 to 7.00. The pH was dependent on the nature of the soil employed.

Frost and Griffin (1977) investigated the adsorption behaviour of arsenic(III), arsenic(V) and selenium(IV) on the clay minerals, kaolinite and montmorillonite. Again, the aqueous carrier selected was municipal solid waste leachate. The researchers used a range of pH values, from pH3 to pH10; they found pH severely influenced the degree of adsorption of all the elements

investigated. Adsorption of arsenic(III) increased with pH, in the pH range quoted. Adsorption of arsenic(V) was maximised at pH5.5, with a subsequent decrease in adsorption at higher levels of pH. Adsorption of selenium(IV) decreased with increase of pH in the range pH3 to pH9. The researchers concluded the disposal of arsenic and selenium in municipal landfills, especially under alkaline conditions could promote groundwater contamination. As mentioned previously, the pH of methanogenic municipal landfills is usually within the range 6.2 to 7.4, one could therefore expect arsenic mobility in that environment.

Reviewing the information above reveals that under aerobic conditions arsenic(V) predominates, in the form of H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-} (Ferguson *et al*, 1972). Under anaerobic, and hence mildly reducing conditions, arsenic(III) predominates (Deuel *et al*, 1972; Hess and Blanchar, 1976). The species of arsenic(III) present under these conditions are H_3AsO_3; $H_2AsO_3^-$; and $HAsO_3^{2-}$ (Ferguson *et al*, 1972). It is evident that these species would predominate within the landfill environment, characterised by neutral pH and mildly reducing conditions. There is conflicting information regarding the mobility of arsenic(III) and arsenic(V). Sadler (1993) states that arsenic(III) has a high mobility in soils; while Elkhatib and co-researchers (1984) report arsenic(III) being irreversibly sorbed by the soils examined, only a small fraction of the arsenic(III) being desorbed from the soils. Korte and co-workers (1976) concludes that arsenic(III) (however, at pH3) was more mobile than other metals examined. Frost and Griffin (1977) found arsenic(V) be mobile, especially at alkaline conditions, while arsenic(III) exhibited an increase in adsorption with rising pH. Shown overleaf in Table 2.14 are details of adsorption studies on municipal solid waste and various type of soils together with a common form of the organic fraction of soils; humic acid.

Table 2.14 Adsorption of arsenic onto municipal solid waste, soils and humic acids

	Study				
	Blakey, 1984	Jones *et al*, 1978	Thanabalasingam *et al*, 1986	Elkhatib *et al*, 1984	Frost *et al*, 1977
Substrate	solid waste	solid waste	humic acids	West Virginia soils	Clay minerals
Test conditions	Anaerobic	Aerobic	_	Aerobic	Aerobic
Liquid	Distilled water	82mM acetic acid	-	Deionised water	Landfill leachate
Arsenic speciation	As(III) and As(V)	As(V)	As(III) and As(V)	As(III)	As(III) and As(V)
Concentration range ($mg\ell^{-1}$)	1.25 - 200	18 - 190	-	5 - 1000	10 - 180 [As(III)] 50 - 650 [As(V)]
Isotherm derived	Freundlich	Langmuir	Langmuir	Freundlich	Non-linear
Dependency of adsorption on pH					
Arsenic(III)	Adsorption increased with pH		Adsorption increased with pH	-	Adsorption increased with pH
Arsenic(V)	Adsorption maxima at pH7	Adsorption decreased with pH	Adsorption maxima at pH5.5	-	Adsorption maxima at pH5.5
Desorption	Arsenic(V): Desorption was less than 5 percent of that adsorbed from aged refuse, the pH range being 5 to 7.	Arsenic(V): Partial or complete desorption, the pH range being 7 to 9.	-	Minimal desorption of arsenic(III)	-

In the case of arsenic(III), there would appear to be agreement that adsorption increases with increase in pH, when considering municipal solid waste, humic acids and the clay minerals.

There is also agreement, that the adsorption of arsenic(V) decreases in an alkaline environment. There is conflicting evidence regarding the relative mobility of arsenic(III) and arsenic(V). It would appear that arsenic(V) is more mobile than arsenic(III), especially above pH5.5.

In general, the adsorption of copper(II) onto soils has been shown to obey the Freundlich isotherm, though the relatively slow rate at which copper(II) is absorbed onto soils makes data from adsorption studies difficult to interpret (Baker, 1990). Aringhieri and co-workers investigated the adsorption kinetics of copper(II) and cadmium(II) on a soil composed of 14 percent organic matter (Aringhieri *et al*, 1985). The initial pH of the solution was 5.4. The initial concentration of the metal ranged from 63.5 to 191$\mu g\ell^{-1}$ for copper and from 56 to 291$\mu g\ell^{-1}$ for cadmium. The mass of soil employed varied from 1 to 3g. Copper exhibited a greater affinity than cadmium to the investigated soil. There was a tendency for copper to form stable organic complexes with organic matter in the soil. Adsorption processes were relatively fast, for both metals. Adsorption was fast for the first 2 minutes, then became slower; after 10 minutes 80 percent of the total adsorption was achieved.

The time dependence curve showed remarkable similarity to those reported by Elkhatib and co-researchers (1984) when they investigated the sorption and desorption of arsenite (arsenic(III)) onto five West Virginian soils. Similar trends were found for copper(II) adsorption by peat soils by Sapek (cited by Aringhieri *et al*, 1985). Sapek suggested from a qualitative viewpoint the adsorption process consisted of two distinct steps: an initial fast adsorption, followed by a much slower adsorption. These modes of adsorption were attributed to an initial rapid diffusion of ions to external soil surfaces, with subsequent diffusion into the inner soil surfaces. The experimental method adopted by Aringhieri and co-workers involved finely divided soil and continuous stirring, an unlikely combination for diffusion to regulate the reaction speed. The researchers reasoned, from examination of the time-concentration curves, the rate of the adsorption process was dependent on: the concentration of the reactive species; the concentration of the substrate in solution and on internal diffusion, which produced a decrease of the specific rate as a function of time.

The adsorption of the two metals was successfully described by the Langmuir isotherm. In the instance where adsorption is successfully described by the Langmuir isotherm, it is possible to represent the sorption process as a reversible first (Gosset *et a*l, 1986; Chen *et al*, 1990; Sharma *et al*, 1993) or second order reaction. This approach proved unsuccessful. The researchers were unable to produce the suitable linear relationship to prove adherence to the rate law. Finally, the researchers reported different rate constants for different concentrations of Cu(II) and Cd(II) possibly, in an effort to provide some numerical form of result. The researchers concluded the rate of adsorption of copper(II) and cadmium(II) onto an organic soil to be dependent on diffusion of the metallic cations through internal surfaces.

Harter reported on the effect of competing ions on the adsorption of copper and lead onto various soils from the northeast of the United States (Harter, 1979). The solution pH was neutral at 7.0; adsorption data was described by the Langmuir adsorption isotherm. Harter observed that an increase in ionic strength of the solution apparently reduced the adsorption of the metallic elements onto the some of the soils, but increased adsorption in others. Unfortunately, conclusions could not be drawn from this. Harter was unsure if imprecise

calculations contributed to these observations. The ionic strength of leachates commonly exceeds 500mSm^{-1}. Information regarding this phenomenon would be useful to apply within the landfill environment. Details of the concentration of copper and lead in solution was not reported. Harter cited work by Irving and Williams (1948) where both copper and lead combined with ligands to form stable metal complexes and chelates. Subsequently, they should form stable complexes with soil organic matter. If one parallels this observation a similar fate should occur to copper within the landfill environment.

Msaky and Calvet (1990) examined the effect of pH within the range 4.5 to 5.5, on the adsorption of copper and zinc onto various soils. It was noted that as the pH value climbed, adsorption increased. This effect is well known and the authors cite a number of examples. Absorption isotherms could be described numerically by the van Bemelen-Freundlich formulation. This was in agreement with the results of other workers. Copper was strongly adsorbed at all pH values. The movement of copper in soil was reviewed by de Haan and Zwerman (1976). The researchers report the mobility of copper in soils to be low, and describe the adsorption of copper onto organic matter, clay minerals, and even pure quartz. Of great interest is a study completed by Lundblad and co-workers (1949). Over 250kg of copper (per hectare) was added to an acid peat soil. After 5 years had elapsed, only 0.2 percent of the copper added was removed from the top 5cm of soil.

Chromium exists in a number of oxidation states, the most common being chromium(III) and chromium(VI). They have sharply contrasting chemical properties. Chromium(III) is much less mobile then chromium(VI) and adsorbs onto particulates more strongly (McGrath *et al*, 1990). Sheppard *et al* (1992) investigated the desorption of heavy metals from a sandy and a clay soil. They also investigated the efficacy of several extracting agents in removing several inorganic trace elements from these soils. One of the eight inorganic trace elements examined was chromium, in the form chromium(VI). The chromium was barely desorbed from a sandy soil. The fixation of chromium was so strong, the authors commented if soil remediation was required, it would be less expensive to remove the soil, as chemical treatment would have to be extensive.

Evaluation of vertical chromium movement in soils has received a high level of attention, particularly sewage treated soils. Some evidence is contradictory, the overwhelming majority of reports have found a general lack of leaching below the zone of sludge incorporation. In one experiment chromium analysis of soils which had received metal contaminated sludge treatment from 1942 to 1961 showed no evidence of significant movement below the depth to which the soil was cultivated (McGrath *et al*, 1990).

2.8.2 Chemical attenuation mechanisms

Chemical attenuation processes include acid-base interactions, oxidation, reduction, precipitation, co-precipitation, ion-exchange, and ion formation.

*(a) **Precipitation and co-precipitation***

When a salt is dissolved in water, there is a limiting amount which can dissolve per unit volume of water. This limiting concentration is called the solubility of the salt in the particular liquid. Additionally, if an excess of salt is added to a liquid, a state of dynamic

equilibrium is achieved between the dissolution of the solid and precipitation of the ions to the solid state (Lowenthal *et al*, 1978). Consider the equilibrium between the solid substance (MX_2), and its aquated ions:

$$MX_2\ (s) \quad \leftrightharpoons \quad M^{2+}\ (aq) \quad + \quad 2X^-\ (aq)$$

The solubility product (K_{sp}), a type of equilibrium constant may be calculated,

$$K_{sp} \text{ for } MX_2 \quad = \quad [M^{2+}]\ [X^-]^2$$

If the solubility product of a particular substance is exceeded, precipitation of the compound occurs until the product of the ionic concentration is less than or equal to value of the solubility product. Co-precipitation may be defined as the simultaneous precipitation of an ion in conjunction with other ion by any mechanism and at any rate (Alloway, 1990).

The solubility of chromium(III) decreases above pH4, and above pH5.5 complete precipitation occurs (McGrath *et al*, 1990). Therefore, chromium(III) would tend to be essentially immobile because of its low solubility. If one considers sewage treated soils, very stable organic complexes account for the very low availability of the element. However, complexing chromium(III) with soluble organic acids, and soil extracts of water-soluble organic matter, maintain chromium(III) in solution at higher pH levels than chromium(III) normally precipitates and hence enhances mobility (McGrath *et al*, 1990). James and Barlett (1983) complexed chromium(III) with soluble organic acids, and soil extracts of water-soluble organic matter, and maintained chromium(III) in solution at higher pH levels higher than 5.5 (above pH5.5 complete precipitation would normally occur). Approximately 25 percent of the chromium(III) added remained in solution at pH6.7. In the complex environment of the landfill these conflicting vectors must be given consideration to evaluate the behaviour of chromium(III).

There are no significant solubility restraints on the concentration of chromium(VI) experienced in pH range normally encountered in the landfill eco-system. However, laboratory studies have shown that chromium(VI) can be readily reduced to chromium(III) in the presence of organic matter, especially at low pH (Calder, 1988). In soils, the presence of soil organic matter can produce the spontaneous reduction of chromium(VI) without regard to pH. In soils incubated with chromium(VI), for four weeks at field capacity moisture, this phenomena was apparent (Bartlett *et al*, 1976). The soil used in the experiment was dried prior to the experiment. This procedure reduces the effects of the soil organic matter (Bartlett *et al*, 1988). The landfill environment abundance of organic matter would have a dramatic effect on the mobility of chromium(VI). The chromium(VI) would be reduced to chromium(III) which then should precipitate from solution. This information is of great value when examining the mobility of chromium(VI) in the landfill environment, it would appear that chromium(VI) would be immobile, but not for similar reasons as copper which were commented on previously.

The mobility of arsenic in soils is increased under reducing conditions, such as flooding soils, because of the increase in the proportion of arsenite (As(III)). Arsenite salts are estimated to be 5 to 10 times more soluble than the corresponding arsenates (As(V)) (Ferguson, 1990).

Unfortunately, low molecular weight organic ligands, not necessarily humic in origin, can form soluble complexes with metals, thus preventing them being adsorbed or precipitated. Of particular concern in the landfill environment is that humic compounds with suitable reactive groups such as carboxyl groups form coordination complexes with metal ions. Carboxyl groups play a predominant role in metal binding in both humic and fulvic acids. The stability constants of chelates with metals tend to be in the following decreasing order:

Cu > Fe = Al > Mn = Co > Zn (Alloway, 1990).

Another factor to consider is the activity of sulphate reducing bacteria in the landfill environment. Hydrogen sulphide is produced by sulphate reducing bacteria, it is a strong reducing agent, and can react and cause the precipitation of metals, such as copper and arsenic. The metals are precipitated as their insoluble sulphides. Arsenic may be co-precipitated with iron sulphide (the iron content of leachates is usually high) or may be directly reduced to arsenic sulphide (cited by Watson-Craik, 1990). In the United Kingdom, regulations allow arsenic in the sulphide form to be co-disposed with municipal solid waste in the ratio of 10kg per tonne of solid waste. In general, arsenical waste may not be co-disposed with municipal solid waste in excess of 10g per tonne (Cossu *et al*, 1989). Ferguson and Gavis (1972) also comment on the strong affinity that arsenic(III) has for sulphur. Kugelman and Chin (1970) state that the most important complexing reaction for controlling toxicity in anaerobic waste treatment is the precipitation of heavy metals as sulphides. Copper is one of the most insoluble of the heavy metal sulphides (Lawrence *et al*, 1965). The table below shows the solubility of copper, and for comparison iron, one of the most soluble.

Table 2.15 Solubility of copper and iron sulphides

(adapted from Lawrence *et al*, 1965)

Metal	Sulphide salt	Solubility Product	Solubility ($mg\ell^{-1}$)
Copper	Cu_2S CuS	2.0×10^{-47} 8.5×10^{-45}	3×10^{-11} 9×10^{-18}
Iron	FeS	3.7×10^{-19}	5×10^{-5}

2.8.3 Environmental aspects of co-disposal

The main problems associated with the co-disposal of industrial wastes with municipal solid wastes may be summarised as follows (Cossu *et al*, 1989):

The inhibiting effect on biological degradation of the municipal solid waste as a consequence of the toxicity of the industrial wastes.

The emission of toxic substances into liquid and gaseous effluent from the landfill, in a higher degree than that from the disposal of municipal solid waste, solely.

The two concerns expressed above are inextricably linked; sterilising the landfill by exceeding the toxicity limit of the various microbial population groups and therefore inhibiting the degradation of the municipal solid waste. The latter aspect can be addressed by noting that a key element of co-disposal is to take advantage of attenuation processes available within the landfill. It must be ensured that wastes to be co-disposed do not overwhelm the landfill eco-system. Emissions from a landfill are not only influenced by the solubility of the various substances but by the interaction of the chemio-physical and biological phenomena. These phenomena can immobilise, degrade and attenuate the mobility of each substance.

An aspect of co-disposal of major importance when considering landfill sterilisation and increase in pollutional aspects is that of "loading rates". Loading rate was defined by the United Kingdom's Waste Management Practices, Landfill Practices Subgroup 2 in 1982 as the maximum quantity of an industrial waste that can be co-disposed with one kilogramme of domestic refuse without adversely affecting leachate quality (cited by Watson-Craik, 1987). As with many statements emanating from the waste disposal establishment in the United Kingdom there is a degree of oversimplification. Values tabulated are not extensive, and those which do exist appear to be extrapolated from past practices. An obvious difficulty is the extreme heterogenous mix of waste arriving at landfill sites, together with the possibility that problems arising from past operations have not yet become apparent.

Rushbrook (1990) collated various maximum loading rates quoted in the United Kingdom, by the various United Kingdom government agencies. These are shown in Table 2.16.

Table 2.16 Co-disposal loading rates

(adapted from Rushbrook,1990)

Constituent	Loading rate	Constituent	Loading rate
Chromium	$100gt^{-1}$	Sulphuric acid	$20kgt^{-1}$
Copper	$100gt^{-1}$	Hydrochloric acid	$5kgt^{-1}$
Lead	$100gt^{-1}$	Phenols	$2kgt^{-1}$
Arsenic	$10gt^{-1}$ $10kgt^{-1}$ (for As in sulphide form)	Oils	$2.5kgt^{-1}$
Mercury	$4gt^{-1}$	Pesticides	20g a.i.* t^{-1}
Cadmium	1kg batteries t^{-1}	PCB	$<50gt^{-1}$
Zinc	$100gt^{-1}$	Cyanide	1g of free CN t^{-1}
Tannery sludge	$66.6kgt^{-1}$		

* a.i. active ingredient

(a) Effect of co-disposal on landfill stabilisation processes

Researchers have investigated the effect of the disposal of industrial wastes with municipal solid wastes. Watson-Craik (1987) examined the co-disposal of phenolic wastewaters with municipal solid waste, while Reinhart (1989) investigated the fate of twelve selected organic compounds, such as dibromomethane, lindane, dieldrin and trichloroethane. It is however inorganic metallic compounds which are of greatest interest in this study. Newton (1977) investigated, at pilot-scale, the co-disposal of a cyanide sludge, an oil water emulsion, and a metal hydroxide sludge containing mainly nickel, chromium and iron. Unfortunately, Newton did not undertake landfill gas measurement, a good indicator of any disruption in the anaerobic degradation process. The leachate composition was examined and the researchers concluded that leachate composition, and hence anaerobic activity, were not obviously affected by the presence of the industrial waste.

Pohland and other workers (Pohland *et al*, 1985; Poland *et al*, 1986a; Gould *et al*, 1989) at the Georgia Institute of Technology, investigated the co-disposal of various metals with municipal solid waste, at pilot-scale. A metal plating sludge containing zinc, chromium, nickel, cadmium, copper and iron was co-disposed with municipal solid waste (Pohland *et al*, 1985 & Pohland *et al*, 1986a) in pilot-scale landfill columns. Four columns were employed. Each column contained 400kg of municipal solid waste. One column was designated a control column (column 1) to which the researchers did not add any metal plating sludge. To the other columns differing amounts of the sludge were added; 33.6kg in column 2; 65.8kg in column 3, and 135.2kg in column 4. The researchers wished to determine the effects of the heavy metals on overall landfill stabilisation and assimilative capacity. Leachate was recycled to enhance stabilisation processes.

The addition of the metal hydroxide sludge slightly elevated the pH of the leachates, but not outside the near neutral range of pH necessary for anaerobic activity. The organic content (COD) of the leachate from control column reduced steadily, as methanogenic conditions were established. This process was slower to be established in column 2 (in comparison to column 1), suggesting some microbial inhibition, with eventual acclimation of the anaerobic bacteria to the heavy metal sludge. In contrast, the organic loading of leachate from columns 3 and 4 remained high throughout the experimental period. This was considered to be direct evidence of interference to the landfill stabilisation processes. The researchers concluded additional research is required to better define limits of heavy metals to be co-disposed with municipal waste.

The co-disposal of mercury, lead, cadmium, chromium, nickel, and zinc with municipal solid waste was also investigated, by largely the same research team (Gould *et al*, 1989). The principal metals of interest being, mercury and lead. The foremost aspect of this study was evaluation of the chemical attenuation mechanisms available, the researchers did not appear to evaluate any disruption to the anaerobic degradation of the municipal solid waste.

An investigation on the impact of grazed pasture by copper, chromium and arsenic timber preservative on soil biological activity (Yeates *et al*, 1994), warrants scrutiny. There is a paucity of data concerning those particular elements, especially in combination. Initially, the researchers visually graded areas of the pasture in terms of heavy metal contamination. Four levels of contamination were graded; uncontaminated, low contamination, medium contamination and highly contaminated. Normal healthy pasture, in a nearby uncontaminated

area, was used as the control. Bare ground was assessed as being highly contaminated. An area displaying stunted, yellowed plant cover was assessed as intermediate or medium contamination. The researchers then sampled the site extensively to determine the degree of contamination, and its variance with depth. The samples were then analysed for metal content. Various biological parameters were measured to ascertain, whether there was evidence of repression of biological activities.

There was a close correlation between heavy metal contamination and the initial visual assessment. All the biological parameters measured in the contaminated area showed correlation with levels of copper, chromium and arsenic. Microbial processes and populations declined with degree of heavy metal contamination. Basal respiration declined significantly at each level of contamination, as did nematode diversity and grouping. Soil decomposition processes were also assessed, and were found to decline with increased levels of contamination. Enzyme activities were investigated. Dehydrogenase, urease, phosphatase and sulphatase activity declined with increased contamination. The researchers concluded that contamination by $100mgkg^{-1}$ of copper, chromium and arsenic caused inconsequential depression of soil biological activity, there was some suppression at $400mgkg^{-1}$, but at $800mgkg^{-1}$ normal biological processes were inhibited and herbage production was negligible. These results were comparable with other workers cited by Yeates and co-researchers.

Wong and Trevors (1988) cite a study completed by Drucker and co-workers. They examined the toxicity of chromium(III) in soil. Chromium(III) was added to soil at concentrations of 10 and $100mgkg^{-1}$; aerobic and anaerobic bacteria were reduced in number. The inhibition of bacterial activity would be detrimental to the establishment of methanogenic conditions in the landfill and hence, increase the mobility of the metallic ions within the landfill environment.

The toxicity of heavy metals in the process of anaerobic digestion is well established and has been extensively investigated by various researchers, principally investigating toxicity effects in waste water anaerobic digesters. An examination of these investigations is advantageous as it is directly applicable to the landfill environment. Studies undertaken at the Robert A. Taft Sanitary Engineering Centre (Barth *et al*, 1965) are often quoted when considering the effects of heavy metals on biological treatment processes. The researchers considered the effects of copper, hexavalent chromium, nickel and zinc, on these processes. The work was carried out at pilot-plant scale, where the effects of heavy metals on the aerobic and anaerobic process, over a ten year period. The researchers found that system response was dramatic, digestion either proceeded normally or ceased entirely. All the metals previously mentioned had a detrimental effect on anaerobic digestion, as measured by an increase in liquid phase chemical oxygen demand, when compared to a control digester.

The role of sulphide, in the prevention of heavy metal toxicity, was thoroughly investigated by Lawrence and co-workers (1965). They investigated the effects of copper, nickel, zinc and iron. They determined that the toxicity of heavy metals was dependent on the concentration in the soluble form, and not on the total concentration in the reaction environment. To determine the toxicity effects, the laboratory scale digesters were first operated with the daily addition of the relevant metals in the sulphate form. This allowed the metals to be precipitated as metal sulphides; the digesters continued to operate successfully. Addition of the metals in form of sulphates was then discontinued. The digesters were then operated

with the addition of the relevant metals in the form of chlorides, thereby eliminating the sulphide precursor. The toxic effects of the metal addition was then observed. The researchers concluded copper, nickel and zinc were toxic to anaerobic digestion, the heavy metals affecting the acid forming bacteria at least as much as the methanogenic bacteria. Ferrous iron was found to be non-toxic, even in the absence of sulphides.

Reid and fellow researchers (1968) evaluated the effects of metallic ions on a number of biological waste treatment processes, amongst them, anaerobic digestion, at laboratory scale. They found that chromium (in the form Cr(VI)) concentrations as high as 85mgℓ^{-1} reduced biogas production by 18 percent, and copper when added in concentrations up to 2mgℓ^{-1}, reduced gas production by 8 percent. Kugelman *et al* (1971) extensively reviewed literature concerning toxic effects in anaerobic waste treatment. The emphasis of the work was the toxic effects of heavy metals. He concluded:

> much of the published data was erroneous and misleading, because of inadequate experimental techniques;
> toxicity effects of heavy metals could be eliminated by sulphide precipitation;
> volatile organic acids are not toxic to methanogens at concentrations less than 6 000mgℓ^{-1};
> a substantial amount of additional research was required.

Mosey and co-researchers (1971, 1975) investigated various factors affecting the availability of heavy metals to inhibit anaerobic digestion, at laboratory scale. One of the conclusions reached was that high chloride ion concentrations could reduce inhibition caused by lead. Both lead and chloride ion concentrations are traditionally high within the landfill environment. Metals shown to be toxic were zinc, cadmium, copper and chromium. It was shown that the toxicity of chromium was similar whether in the trivalent or hexavalent form.

Hayes *et al* (1978) principally examined the distribution of heavy metals among the soluble, precipitated extracellular, and intercellular components, using laboratory scale anaerobic digesters. The effects of metal addition on anaerobic digestion were also collated. The metals examined included, cadmium, chromium(VI), chromium(III), copper, lead, nickel, and zinc. The digesters were dosed with the metals in a step- and pulse-like fashion. Metal addition in a pulse-like mode is akin to shock loading, while metal addition in a step-like manner allows microbial acclimation to the addition of the metal. The inhibitory level of a heavy metal was defined as that time, when any decrease in gas production became evident. Toxic levels were taken to be that concentration at which gas production was reduced by 70 percent. The results are shown overleaf in Table 2.17.

The general ranking of heavy metal toxicity for those metals investigated was;
Ni > Cu >> Cr(VI) ≈ Cr(III) > Pb > Zn. Cadmium did not have any noticeable effect at concentrations used in the experimental study.

Table 2.17 Heavy metal toxicity limits for anaerobic digestion

(adapted from Hayes *et al*, 1978)

Heavy metal	Step-fed		Pulse-fed
	Inhibiting concentration ($mg\ell^{-1}$)	Toxic limit ($mg\ell^{-1}$)	Toxic limit ($mg\ell^{-1}$)
Chromium(III)	130	260	<200
Chromium(VI)	110	420	<180
Copper	40	70	<50
Nickel	10	30	>30
Cadmium	-	>20	>10
Lead	340	>340	>250
Zinc	400	600	<1 700

(b) Effect of co-disposal on leachate composition

The effect of co-disposal on leachate composition at pilot-scale and full scale operations are well documented by various researchers. The work undertaken by Pohland and his fellow workers has already been referred to in Section 2.8.3(a). The researchers co-disposed a heavy metal hydroxide sludge containing zinc, chromium, nickel, cadmium, copper and iron with municipal solid waste, at pilot-scale. They found when metal addition exceeded a certain level, anaerobic activity was inhibited and the organic content of the leachate was not reduced with time. Levels of zinc, cadmium and nickel, in leachate from the columns were also affected detrimentally. Levels of zinc, cadmium and nickel in leachate from the column where co-disposal was not practised (column 1) and the column where the lowest amount of metal sludge was added (column 2) were described as "inconsequential". Leachate from the heavier loaded columns (columns 3 and 4) contained nickel, cadmium and zinc at levels higher than columns 1 and 2. Zinc was present at levels generally considered to be inhibitory to anaerobic digestion in the leachate from columns 3 and 4.

Levine *et al* (1989) evaluated leachate monitoring data from co-disposal, hazardous and sanitary waste disposal sites located in the United States. The researchers examined data from a total of 1 560 samples from 58 facilities over the period, 1984 through 1987. The data was supplied from 88 co-disposal sites, 90 hazardous waste sites, and 49 sanitary landfills. The table shown below (Table 2.18) is adapted from their results.

Table 2.18 Metals detected in leachates from co-disposal, hazardous and municipal landfill leachates

(adapted from Levine *et al,* 1989)

Landfill	**Co-disposal**	**Hazardous**	**Municipal**
Metal	Mean value ($\mu g \ell^{-1}$)	Mean value ($\mu g \ell^{-1}$)	Mean value ($\mu g \ell^{-1}$)
Arsenic	33	507	14
Total chromium	138	215	57
Hexavalent chromium	104	303	149
Copper	46	268	35
Lead	76	79	48
Mercury	1	3	1
Nickel	272	1264	137
Zinc	1202	1085	791

Analyses of leachate from the hazardous waste landfill sites showed metal levels in the leachate far above the co-disposal sites and the municipal sites. Co-disposal leachate is, on average, higher in metallic contamination than that from the municipal sites. For comparative purposes data reported from the United Kingdom is shown below in Table 2.19.

Table 2.19 Composition of leachates from different classes of landfills

(adapted from DOE, 1986)

Metal	**Household**	**43 percent Industrial**
Chromium	0.05 - 1.0	0.05
Iron	0.1 - 2050	10
Nickel	0.05 - 1.7	0.04
Cobalt	0.01 - 0.15	0.09
Zinc	0.05 - 130	0.16
Cadmium	0.005 - 0.01	0.02
Lead	0.05 - 0.6	0.10

(all results in $mg\ell^{-1}$)

It can be seen (in Table 2.19), with the exception of cadmium, all of the metals shown occur in higher concentrations in leachate from landfill where only municipal solid waste is disposed. Two factors should be considered when comparing this data from the United States and the United Kingdom. The authorities in the United Kingdom are very strong supporter of co-disposal; figures concerning leachate composition are extremely variable.

Assmuth (1992) conducted a 5 year study (1985-1990) examining 43 sites in southern and central Finland. The landfills examined may be defined as co-disposal. Wastes now defined as hazardous in Finland, were disposed in an uncontrolled manner, in local municipal landfill sites. Assmuth examined leachate composition, solid waste composition, interstitial water composition, and landfill gas composition. Assmuth reported considerable variance of attenuation mechanisms, but considered the environmental toxicological risks from municipal co-disposal leachates to be small when compared with the impacts and risks from other sources. Assmuth considered the transport of both metals and organic contaminants such as dichloromethane, total xylenes, etc., and considered the attenuation of heavy metals was the greatest. Assmuth mentions the precipitation tendency of metallic ions at prevailing pH levels within the landfill environment. This statement is only partially correct, as some metals (obvious examples being arsenic(V), arsenic(III) or chromium(VI)) would not precipitate directly at the pH range operating within a landfill. From the examination of the behaviour of these metals in soils (Section 2.8.1.3(d)) adsorption would surely provide a significant reduction of the concentration, of these metals, in solution.

As stated previously, Assmuth examined the concentration of different fractions in solid waste samples, extracting metals with both strong and weak acids. The most easily extracted metals were lead and zinc; chromium, copper, arsenic, and nickel (in order of increasing mobility); being more strongly bound in the waste matrix. This work was confirmed by laboratory analyses of the leachate from the landfill sites. Zinc was found in the highest concentration in leachate from the landfills examined. Lead is probably precipitated as lead chloride, confirming work reported by Mosey and co-workers (Mosey *et al*, 1971) when investigating the ability of heavy metals to inhibit anaerobic digestion at laboratory scale (2.8.3(a)). Although zinc is strongly adsorbed by clays and organic matter, the presence of soluble organic matter, such as fulvic acids, which are soluble over a wide range of pH, can greatly increase the solubility and mobility of zinc (Kiekens, 1990). Researchers investigating leachate from soil have found 60-75 percent of the total soluble zinc present was in the form of soluble organic complexes (Kiekens, 1990).

In a companion study (Assmuth *et al*, 1993) sampled groundwater at 16 co-disposal landfill sites. It was found that some impairment of groundwater quality was notable at almost all of the sites examined. However, in some of the cases, that impairment could have been caused by other factors other than those related to landfills. Frequently, heavy metals were in abundance in the groundwater, the median value for zinc being 80ppb. Black *et al*, (1989) evaluated the environmental hazard presented by two large metropolitan landfills located near New York, in the United States. These landfills received both municipal and commercial waste in an uncontrolled manner. Data is presented on airborne contaminants, sediments and the water bodies surrounding the two landfills. The researchers concentrated mainly on pollution from certain classes of organic chemicals. However, copper was present in seepage samples at levels of 38-46$\mu g \ell^{-1}$, and 6-16$\mu g \ell^{-1}$ copper, was found in Jamaica Bay, an

adjoining body of water. Copper in seawater usually approximates 0.04-0.1$\mu g\ell^{-1}$ (Forstner *et al*, 1979).

Newton (Newton, 1977; DOE, 1975; Knox *et al*, 1990) conducted pilot-scale and laboratory scale investigations, where he co-disposed three types of industrial wastes with municipal solid waste. The wastes studied were an aqueous oil emulsion, a cyanide heat treatment waste and a metal-hydroxide sludge. The metal hydroxide sludge was obtained from the effluent treatment plant of a plating works. The vessels were placed outdoors and subjected to natural rainfall. The sludge was composed principally of nickel and chromium, though small quantities of zinc, copper, lead and cadmium were present. Unfortunately, the researchers did not undertake landfill gas measurements. The experiment was terminated after three years. During this period concentrations of cadmium, copper and zinc in the leachate did not increase, however, the nickel concentration rose to 51$mg\ell^{-1}$, and the chromium concentration rose to 5.7$mg\ell^{-1}$. This was believed be acceptable by the researchers.

Knox and Gronow (1990) compiled and reviewed data gathered concerning anaerobic digesters, laboratory scale experiments, pilot-scale studies and activities at full-scale landfills. The data is conveniently segregated into four groups of compounds co-disposed with municipal solid waste. These are; phenols, cyanides, acids and heavy metals. The researchers considered the landfill to be a stationary fixed film reactor. They compare range and loading of waste inputs, while concomitantly examining effluent (leachate) quality. The six most studied metals were zinc, copper, nickel, chromium, lead, and cadmium. The data examined was derived from twelve projects based in the United States, United Kingdom, and Hong Kong. Of the twelve experimental projects, ten were laboratory or pilot-scale column studies, two of the experimental studies were equilibrium tests.

The researchers commented that the attainment of methanogenic conditions appeared to be of importance. In one study, nickel was added to two reactors at approximately 157mg per kilogram of solid waste. The nickel content of the leachate of the acetogenic reactor rose to 86$mg\ell^{-1}$ while in the methanogenic reactor the nickel content did not exceed 0.46$mg\ell^{-1}$. It is probably physio-chemical effects which predominate in this instance. The higher, near neutral pH commonly experienced with methanogenic activity, in comparison with the lower pH, associated with acetogenic activity. The metallic compounds mobility being enhanced at the lower pH.

Few of the studies reviewed by the researchers directly examined the effects of metal loadings on the biological processes; however, leachate composition was obviously noted. Where the metals had been added as metallic sludges the leachates showed little enhancement of leachate metal concentration. Experiments where the metals were added in solution, showed elevated metal concentration. It is probable the pH effect was being demonstrated here, the alkali content of the metal sludge, reducing metal ion mobility. Of interest, two studies reported enhanced metal content with leachate organic content. Where methanogenic conditions were established, there was insufficient evidence of inhibition, caused by the presence of heavy metals. The researchers evaluated data from five full scale landfill sites operated in the United Kingdom. Where methanogenic conditions were firmly established, there was no inhibition of methanogenic activity. However, even with the additional loading of heavy metals by co-disposal with the municipal solid waste, the sum of the applied metals plus those

metals associated intrinsically with the municipal solid waste did not exceed the values commonly reported to be inhibitory in anaerobic digesters.

(c) Effect of co-disposal on landfill gas composition

Early efforts to evaluate gaseous emissions from landfills were primarily concerned with methane and the associated dangers of explosions, fires, and potential asphyxiation of surrounding residents in their homes (Rickabaugh *et al*, 1993). Recent measurements at landfills in the United Kingdom, indicate workers may be exposed to concentrations of toxic substances which exceed United Kingdom Occupational Health Legislation (cited by DOE, 1990). Researchers have concentrated on the emission of volatile organic compounds (Deipser *et al*, 1994; Rickabaugh *et al*, 1993), although when Blakey (1984) investigated the behaviour of arsenical wastes when co-disposed with municipal solid waste. He noted that under anaerobic conditions, arsenic compounds are reduced and methylated to di- and tri-methylarsine by a number of species of anaerobic bacteria. However, the production of arsine is the primary mechanism for gaseous loss of arsenicals from soils when compared to methylation. Blakey expressed concern on the migration of volatile arsenical species into the gaseous emissions from the landfill. Elfving and co-researchers (1994) cite an example where biomethylation of arsenic and the evolution of methylarsine occurred. The removal of arsenic by bioremediation, from soils contaminated by lead arsenate has been accomplished by adding apple pomace as a carbon source, and flooding the surrounding area to establish anaerobic conditions.

An extreme example of the effect of co-disposal on the composition of the biogas has been reported from the United Kingdom (DOE, 1986). The hydrogen sulphide concentration of the biogas exceeded 30 percent. Hydrogen sulphide concentrations do not normally exceed 10 ppm in landfill gas. In this case, gas emitted from the landfill presented a considerable hazard to workers at the site. The problem was traced to the presence, within the landfill, of material containing high concentrations of sulphate. Arsine generation has also been reported when cover material containing arsenic was utilised at another landfill site in the United Kingdom (DOE, 1986). Several toxic metals were co-disposed with municipal solid waste in pilot-scale landfills at the Georgia Institute of Technology (Pohland *et al*, 1986a; Gould *et al*, 1989). The metals examined were mercury, lead, zinc, chromium, nickel, cadmium, copper, and iron. The researchers concluded that mercury was reduced to the neutral metal and that would facilitate the volatilisation of the metal which would then be transported in the gas phase leaving the landfill.

2.9 THE HEAVY METALS UNDER EXAMINATION: COPPER, CHROMIUM AND ARSENIC

The metallic elements of concern to this investigation are copper, chromium and arsenic. These metals are in common use in combination, as a water based wood preservative, traditionally named CCA, or Tanalith. The preservative commonly consists of a mixture of copper in the form of its sulphate salt ($CuSO_4$); chromium, in the form of sodium dichromate ($Na_2Cr_2O_7$) and arsenic in the form of arsenic pentoxide (As_2O_5). Copper and arsenic are the principal pesticidal agents, whereas the purpose of the chromium salt is to affix the two

former compounds within the wood (DOE, 1980). It is advantageous to consider each of the reagents of this formulation separately, then to consider the mixture in its entirety.

2.9.1 Copper

Copper (Cu) is the first element of subgroup IB of the Periodic Table. Copper has an atomic number of 29 and an atomic weight of 63.546. The effects of copper pollution in rivers was examined by researchers in western Wales, in the United Kingdom (cited by Gaufin, 1974). The River Dove was examined. It was found to be contaminated by organic matter, but appeared to be recovering a few miles downstream. A discharge of industrial effluent to the waterway then occurred. Industrial effluent from a copper processing plant was discharged into the river, the average copper content in the river was raised to 1ppm and above. This discharge had an extremely stressful result on the river ecosystem. All the animals, which above the copper processing plant consisted of Tubificidae, *Chironomus*, *Asellus*, leeches and mollusks, disappeared. None were found in the next 11 miles to the confluence with the Dove, where the copper content had fallen to 0.6ppm. Algae were also seriously effected.

Under normal conditions copper is benign agent for humans. The total body copper content of a human is about 100-150mg, a normal diet provides 1-5mg of copper per day. It is reported to be difficult to formulate a diet with less than 1mg of copper per day (Baker, 1990). There are however, examples in the literature of copper poisoning (Forstner *et al*, 1979). An example cited by Forstner concerns the poisoning of fish off the coast of Holland in 1965. Innumerable dead fish, of widely diversified species, were found between Scheveningen and Ijmuiden. It was established the seawater contained a concentration of copper as copper(II) of several hundred micrograms per litre. The normal concentration varies from 1-3 micrograms per litre. The source of the copper pollution was only found accidentally; several kilograms of copper sulphate crystals were found buried under sand near Noordwijk. Copper, in the form of copper sulphate, is used extensively for the prevention of algal growths, especially in and around swimming pools (Perkins, 1978). It is one of five metals on the EPA list of most commonly discharged priority pollutants (cited by Novotny, 1995). The other most commonly discharged priority pollutants are zinc, chromium, lead and nickel.

2.9.2 Chromium

Chromium (Cr) is a *d*-block transition metal of Group VIB, of the Periodic Table. Chromium has an atomic number of 24 and an atomic weight of 51.996. Chromium has been used in alloy steels since about 1877. Chrome plating commenced in approximately 1926. It is resistant to oxidation and its used industrially in alloys which are resistant to corrosion. It usually occurs in +3 and +6 oxidation states in the environment, though Chromium(III) is the most stable state (McGrath *et al*, 1990).

Chromium is one of the least toxic of the heavy metals. In general, the mammalian body can tolerate 100 to 200 times its normal total body content of chromium without harmful effects. Chromium(VI) compounds are, in general, approximately 100 times more toxic than chromium(III) salts. Stomach acidity reduces chromium(VI) to chromium(III), gastro-intestinal absorption of chromium(III) is less than 1 percent of that of chromium(VI) (Forstner

et al, 1979). The link between occupational exposure to chromates and the increased risk of lung cancer is well established. Over a century has passed since Newman reported a case of nasal cancer in a chrome pigment worker in 1890 (cited by Yassi *et al*, 1988). Later in 1936, German health authorities accepted that lung cancer in chromate producing workers as an occupational disease. Authorities in the United States concurred 10 years later.

Forstner *et al* (1979) quotes an example of catastrophic heavy metal poisoning concerning chromium, that occurred in the early 1970's around Tokyo, Japan. The Nippon Chemical Industry Company deposited approximately 530 000 tonnes of unreduced slimes and wastes containing hexavalent chromium; the waste material gained extensive use in construction projects. Additionally, complete housing blocks along Tokyo Bay have been erected upon spoil heaps containing toxic chromium(VI) compounds. The extent of the tragedy had not been completely evaluated at the time of writing (1979), official figures at that time revealed 30 dead, 200 people incurably ill. Investigations of groundwater near the deposits contained more than 2 000 times the official limit. More alarming still, the effluent from the Nagoya municipal wastewater treatment plant turned yellow. Chromium is one of five metals in the EPA list of the most commonly discharged priority pollutants (cited by Novotny, 1995), the others being zinc, copper, lead and nickel.

2.9.3 Arsenic

Arsenic(As) is a metalloid, located in Group VB of the Periodic Table. Arsenic has an atomic number of 33 and an atomic weight of 74.9216. Elemental arsenic exists as a metallic modification commonly called grey arsenic, as well as a non-metallic modification commonly called, yellow arsenic (Seinko *et al*, 1966). Over 200 arsenic containing minerals have been identified, approximately 60 percent being arsenates, 20 percent being sulphides and sulphosalts, the remaining 20 percent, arsenides, arsenites, oxides, and elemental arsenic. The most common of the various forms of arsenic is arsenopyrite, the chemical formula being FeAsS (O'Neill, 1990).

Arsenic occurs in most frequently in nature in the pentavalent state as arsenate. It is in this form it has been applied as an insecticide, usually in the form of lead arsenate. Many orchards in Missouri, United States, have been treated with lead arsenate for 20 to 80 years causing the arsenic concentration in the soil be in excess of 100 ppm (Hess *et al*, 1976). Sadler and fellow workers (1992) quote examples of orchard sites with maximal soil arsenic concentrations of 124 238 and 2 000$mgkg^{-1}$ at three different sites. This gross contamination must be seen against naturally occurring or background levels of arsenic in the environment. For water the expected range is 0.01 to 1$mg\ell^{-1}$, for soil, 1 to 500$mgkg^{-1}$, 0.1 to 1.6$mgkg^{-1}$ for grass, 0.01 to 0.05$mg\ell^{-1}$ for milk and 0.06 to 1.1$mgkg^{-1}$ for meat (Onken *et al*, 1995). Arsenic in aquatic systems has a complex chemistry, reactions involving oxidation-precipitation, ligand exchange, precipitation and adsorption, all take place. It is stable in four oxidation states, namely, +5, +3, 0, -3, under conditions occurring in aquatic systems (Ferguson *et al*, 1972). The toxicity of arsenic varies with its oxidation states, trivalent arsenic is of substantially greater toxicity then pentavalent arsenic (Thomas, 1994). Ghosh *et al* (1987) specify the toxicity scale of arsenic as follows:

Arsine > arsenite > arsenate > alkyl arsenic.

Abernathy *et al* (1992) report a number of catastrophic episodes involving arsenical compounds. In the United Kingdom, during 1900, sugar contaminated by arsenic was used in the production of beer. This resulted in the deaths of more than 70 people, and illness occurred in a further 6 000. This resulted in the formation of a Royal Commission of Inquiry. The Commission found that the malt had been contaminated to dangerous levels, from the arsenical content of the coal fuel used in the kiln (Brame *et al*, 1961). One death occurred in Virginia, United States, coupled with illness in eight other family members. The cause, of significance in this investigation, was contaminated groundwater. An average person of mass, 70kg, contains approximately 10mg of Arsenic. The human liver continually extracts arsenic, converting it to mainly dimethylarsinic acid, this then is excreted by the body in urine. This methylated version of arsenic has only 1 percent of the toxicity of inorganic arsenic in the form arsenic(III) (Emsley, 1985).

2.10 THE COPPER-CHROMIUM-ARSENIC WOOD PRESERVATIVE

Wood, a raw material of biological origin, is vulnerable to attack by bacteria, fungi, insects and marine borers. Treatment by a suitable agent can considerably reduce the deterioration of the original product. Timber preservation is practised globally and it is an important component of the forest products industry. In 1990, there were approximately 3 300 pressure-treatment plants operating in the world, their production is estimated at 30 000 000 m^3 of timber products per annum. The global nature of the industry is illustrated in Table 2.20 below (cited by UNEP, 1994).

Table 2.20 Major producers and product rates of preservative treated wood
(cited by UNEP, 1994)

Country or Area	Production of preservative treated wood ($m^3 annum^{-1}$)	Country or Area	Production of preservative treated wood ($m^3 annum^{-1}$)
France (1988)	219 000	South Africa (1988)	430 000
Germany/FRG (1988)	1 000 000	Japan (1988)	408 000
Scandinavia & Finland (1989)	1 369 000	Australia (1988)	942 000
United Kingdom (1989)	1 968 000	New Zealand (1986-87)	1 460 000
USA (1988)	16 009 000		

The total production of the various chemicals used for wood preservation is estimated to be excess of 550 000 tonnes per annum. There are three principal preservatives; a waterborne preservative; an organic solvent, and various tar oils, composed of mainly creosote. The distribution of their production is as follows:

Category	**Production**
Tar oil	350 000 tonnes per annum
Waterborne	90 000 tonnes per annum
Organic solvent	110 000 000 litres per annum

Copper-chromium-arsenic (CCA) is grouped within the waterborne preservatives. The initial formulation was first patented by S. Kamesam in 1933 and is known as *Ascu*. This first formulation was composed of 55 percent potassium dichromate ($K_2Cr_2O_7$), 33 percent copper sulphate (as $CuSO_4.5H_20$) and 12 percent arsenic pentoxide (as $As_2O_5.2H_2O$). This formulation resembled the acid copper chromate commercially known as *Celcure* which had been in use since 1927. The primary difference being that a proportion of the copper sulphate was replaced by arsenic pentoxide.

A number of different parties used similar preparations. From 1936 to 1948 the Boliden Mining Company in Sweden produced wood preservation products called *Boliden BIS* and *Boliden S25*. The former was a zinc-chromium-arsenic formulation, the latter a zinc-copper-chromium-arsenic formulation. Unfortunately, these products were not as successful as the original *Ascu* product they were modelled on. The lower chromium content allowed easier leaching under adverse conditions. Boliden marketed a copper-chromium-arsenic product with the various elements in the form of their oxides, probably to avoid infringement of Kamesan's *Ascu* patent. In the United States, the Bell Telephone Company released results of a survey of telephone pole treatment, in 1942. The preservative developed was called *Greensalt*, a product similar to *Ascu*. During this period in the United Kingdom, the original *Ascu* was replaced by *Celcure "A"* and *Tanalith "C"*, both copper-chrome-arsenic products (Hickin, 1971).

The chemicals under discussion, by their very nature, and their toxicity to living organisms, can be hazardous to personnel handling them, the general public should they inadvertently come into contact with them, and to the environment at large.

2.11 THE DISPOSAL OF COPPER-CHROMIUM-ARSENIC TREATED WOOD PRODUCTS

This subject is currently a controversial topic amongst researchers, regulatory organisations and interested pressure groups. In the United Kingdom, the Department of Environment is a protagonist of a liberal viewpoint, in line with the philosophy of "dilute and disperse". It would be apt to outline their policies as stated in Waste Management Paper No, 16: Wood-preserving wastes (DOE, 1980).

It was estimated in 1970-72 approximately 11 000 tonnes of inorganic salts were required for the annual production of the waterborne preservatives, the most common type being the CCA

wood preservative. Of this, approximately 1 370 tonnes were consumed in the United Kingdom, the remainder being exported. The primary use, over 50 percent, is the treatment of building timbers, 20 percent is used to treat fencing, the remainder mainly miscellaneous industrial applications. Also, at that time, the amount of timber treated by all wood-preservation methods was estimated at $2Mm^3$. In 1988, analysts Jermer and Evans (cited by UNEP, 1994) quoted the figure of 1 968 $000m^3annum^{-1}$, it would appear from this that statistics quoted in 1970 could be relatively unchanged, and are good indicators of usage and disposal today in the United Kingdom.

Details are supplied by the Department of the Environment regarding the usual treatment specifications for the CCA treatment of new wood. The specifications vary with respect to the intended end use of the wood. The treatment of building and fencing timber typically relates to a minimum 1.4kg of arsenic (approximately 5kg total salt) per tonne of wood. For cooling tower internals or marine timbers this relates to 6kg of arsenic (approximately 10 kg total salt) per tonne of wood. Approximately half of the arsenic can be lost during service, however, a typical tower may contain between 200 and 350 tonnes of packing. From approximations such as these, various indicators for future waste disposal are estimated. However, it is stated in the document the very reasonable conclusion that at a future date the annual arisings from demolitions etc., will equate to current treatment levels of 1370 tonnes of CCA salt, or 500 tonnes of arsenic per annum.

Open burning of wood from demolished buildings in the United Kingdom was, in 1980, a widely used disposal method for CCA-treated wood. The Department of the Environment recommended the continuation of this practice with the *proviso* that the wood should be burnt at least 100m from continuously occupied buildings; not more than half a tonne of wood be burnt at any one fire; not more than one tonne of wood per day be burnt any single site. The burning of cooling tower fill, in open fires, was also a widely used disposal method. The Department forbids the disposal of cooling tower fill and marine timber by burning in open fires as the CCA salt content is approximately triple that of building materials (see above) and suggested disposal in a suitably designed incinerator. If these disposal routes were not available, it was thought the CCA-treated wood could be placed in an appropriate landfill site. As the copper, chromium and arsenic are *securely* bound within the wood, there is no requirement for restriction. Wood regardless of species is composed of two principal materials: cellulose, which is approximately 70 percent of the volume, and lignin, nature's glue for holding the cells and fibres together (Clauser *et al*, 1963). The remainder is composed of minerals, waxes, tannins, oils, etc.

The United States Public Health Service (1970) initiated two research projects into composting in 1953, one of the projects in Savannah, Georgia, determined chemical composition of municipal solid waste; researchers were interested in changes that occur during the composting process. Barlaz also addressed the chemical composition of municipal solid waste (Barlaz, 1988) when determining the contribution of the various fractions of municipal solid waste to methane production. Rees (cited by Watson-Craik, 1987) provided analyses of the chemical composition of municipal solid waste from two representative locations. Results from their studies are tabulated overleaf in Table 2.21.

Table 2.21 Chemical composition of municipal solid waste

Savannah, Georgia, 1958		Barlaz, 1988		Rees, 1985		
Component	% dry weight	Component	% dry weight	Component	% dry weight	% dry weight
Lipids (ether soluble)	10.1	Cellulose	51.2	Cellulose	35.1	37.1
Crude fibre	35.9	Hemi-cellulose	11.9	Hemi-cellulose	1.6	4.4
Total sugar	4.9	Protein	4.2	Protein	5.8	5.6
Starch	8.1	Lignin	15.2	Lignin	7.6	8.5
Protein (6.25N)	8.2	Starch	0.5	Starch	0.3	0.4
Volatile solids	92.2	Pectin	< 3.0	Lipids	< 0.1	< 0.1
		Soluble sugars	0.35	Soluble sugars	0.4	0.7
		Volatile solids	78.6	Volatile solids	50.9	56.8

It can be seen the combined cellulose and hemi-cellulose content of municipal solid waste range from approximately 40 to 60 percent. One could therefore expect excellent adsorption of CCA within the landfill environment. However, as often occurs, conflicting reports can be quoted. Sadler and co-workers (1994) refer to soil in contact with wood treated with CCA. Observed arsenic soil residues ranged from 70 to 220mgkg^{-1}. This would not seem to indicate secure adsorption within the wood.

The American Wood Preserves Institute (AWPI) has a home page on the Internet where it addresses the issue of the life cycle of pressure-treated wood (http://www.awpi.org, 1996). A document of several pages is available for electronic perusal. Treated wood products in the United States can be regulated at federal, state, or by local juristriction. The document refers mainly to Federal Law, though caution that users should conform to local and state requirements.

The treated wood product is covered by distinctly different regulations than the chemical utilised for wood treatment. The chemicals such as CCA are regulated by the **F**ederal **I**nsecticide, **F**ungicide and **R**odenticide **A**ct (FIFRA). Additionally, treated wood waste has

not been treated as a hazardous waste under the Federal **R**esource **C**onservation and **R**ecovery **A**ct (RCRA). In 1992, the EPA published in the Federal register that arsenical-treated wood products disposed of by the end user are exempt from classification as a hazardous waste, regardless of results from the **T**otal **C**haracteristic **L**eaching **P**rocedure (TCLP) for specified constituents from any individual sample. Nevertheless, if the wood product exceeded regulatory requirements for any other constituent it would forgo it's exemption. Therefore, as a non-hazardous material pressure treated wood by CCA may generally be disposed at municipal landfills. The EPA publish consumer information sheets containing data on the disposal of pressure-treated wood. Consumers are warned never to dispose of treated wood by means of open fires.

The **I**ndustry and **E**nvironmental **P**rogramme **A**ctivity **C**entre (IEPAC) operating under the umbrella of the United Nations is concerned about the disposal of treated timber (UNEP, 1994). The amount of timber being treated globally continues to rise, at present over 30 million cubic metres of wood are being industrially treated, and after 30 years, disposal will then be required. It comments that current disposal options are not encouraging, uncontrolled burning is *out of the question*, incineration of such volumes *impractical*, and disposing to landfill is *not encouraging*.

2.12 SUMMARY

Globally, volumes of solid waste (both industrial and municipal) continue to increase. A developing country such as South Africa strives for a higher standard of living for its citizens. A higher standard of living has always been associated with greater consumption of energy and resources, resulting in a larger production of waste materials. Co-disposal of hazardous chemicals with municipal solid waste is practised in South Africa, in suitably constructed containment landfills. However, even with a contained landfill, leachate will be produced and will require treatment either prior to discharge to the municipal sewerage system, or to a suitable waterway. When co-disposal is practised, it is of importance that the emission of toxic substances from the landfill is not increased to levels that can be detrimental to the surrounding environment. There is a paucity of available data concerning co-disposal ratios and much of the information is conflicting and causes confusion.

The material of concern in this investigation is a wood preservative commonly called CCA, or Tanalith. The preservative consists of a mixture of copper, chromium and arsenic. These chemicals, either individually, or in combination, can be hazardous to personnel handling them, to the general public, and to the environment. The disposal of these substances, both as waste solution, and in combination with wood at the end of its lifecycle, has become a matter of concern to such august organisations as IEPAC. The objective of this current study is the development of guidelines for the disposal of CCA within the landfill without any additional degradation of the surrounding environment.

CHAPTER 3
THEORETICAL CONSIDERATIONS

3.1 INTRODUCTION

The concepts of adsorption isotherms, chemical kinetics and tracer response analysis, are employed throughout the investigation into the immobilisation of copper, chromium and arsenic in stabilised domestic refuse. These concepts are discussed below.

3.2 ADSORPTION ISOTHERMS

An adsorption isotherm represents the functional relationship between the adsorbed phase concentration, and the fluid phase concentration of the solute, at equilibrium. There are four main adsorption isotherms: the Freundlich isotherm, the Langmuir isotherm; the BET (Brunaer, Emmett, and Teller) and the Gibbs Isotherm (Tan, 1993). The two most commonly used adsorption isotherms are the Langmuir and Freundlich isotherms, which were first introduced approximately 70 years ago. The success of these isotherms reflects their ability to fit a wide variety of adsorption data quite well. It may also partly reflect the appealing simplicity of the isotherm equations and the ease with which their adjustable parameters can be estimated. Both isotherm equations can be transformed to a linear form and so their two adjustable parameters are easily estimated by graphical means, or by linear regression (Kinniburg, 1986). It is however, important to note, like empirical rate laws, adsorption isotherms equations cannot be interpreted to indicate any particular adsorption mechanism, or even if adsorption, *as opposed to precipitation, has actually occurred* (Sposito, 1989). Data presented in Chapter 5 is described by the Freundlich Isotherm, but as reference is made in the text to the Langmuir Isotherm, both are described below.

3.2.1 Freundlich Isotherm

The Freundlich isotherm is not derived from theoretical concepts but is based on empirical relationships. It does however, have the ability to describe adsorption data obtained at constant temperature (Sposito, 1980). The equation has often been associated with adsorption by heterogeneous surfaces (Tan, 1993). It may be expressed as (Malina, Jr., 1967):

$$q = K_F C_e^M \qquad 3.1$$

Where,

q	=	solute adsorbed per unit weight of solid adsorbent
K_F	=	Freundlich equilibrium distribution coefficient
C_e	=	Concentration of solute remaining in fluid at equilibrium
M	=	Freundlich power coefficient

Data are usually fitted to the logarithmic form of the equation:

$$\ln(q) = M \ln(C_e) + \ln(K_F)$$

If the Freundlich adsorption isotherm is suitable, a logarithmic plot of solute adsorbed (q) versus equilibrium solute fluid concentration (C_e) results in a straight line with a slope equal to the Freundlich power coefficient (M) and an intercept equal to the value of the logarithmic form of the Freundlich equilibrium distribution coefficient (K_F). The Freundlich equilibrium distribution coefficient may be considered as a measure of affinity (Murali *et al*, 1983).

Numerous examples exist in the literature where the Freundlich isotherm has been used to describe the adsorption of solutes by a solid matrix. Smith (1981) cites as examples, the adsorption of; hydrogen gas on tungsten and aqueous sulphur dioxide on activated carbon. Examples involving the adsorption of solutes onto the soil matrix abound (Travis *et al*, 1981). In an excellent survey of sorption relationships in soil, Travis and Etnier (1981) cite more than 30 examples of the adsorption of various solutes onto the soil matrix where the Freundlich equation has described the adsorptive process. The solutes diverge from anions such as sulphate, metallic ions, to herbicides, pesticides and various hydrocarbons.

3.2.2 Langmuir Isotherm

The Langmuir equation for isothermal adsorption may be deduced from kinetic considerations or from the thermodynamics of adsorption. It is based on the following assumptions:

(1) Maximum adsorption corresponds to a saturated monolayer of solute molecules on the surface of the adsorbent;
(2) Energy of adsorption is constant at all adsorption sites;
(3) No transmigration of adsorbed molecules in the plane of the surface.

The Langmuir equation may be written as (Murali *et al*, 1983):

$$q = \frac{K_L C_e Q}{(1 + K_L C_e)} \qquad 3.2$$

Where,

q = solute adsorbed per unit weight of solid adsorbent
K_L = Langmuir equilibrium distribution coefficient
C_e = Concentration of solute remaining in fluid at equilibrium
Q = Adsorption capacity

A convenient linearised form of the Langmuir equation is,

$$\frac{1}{q} = \frac{1}{Q} + \frac{1}{K_L C_e Q} \qquad 3.2(a)$$

If the Langmuir isotherm is obeyed, a plot of $1/q$ versus $1/C_e$ the intercept at $1/C_e = 0$, allows the calculation of the reciprocal of the Adsorption capacity (Q). The Langmuir equilibrium distribution coefficient (K_L) is a measure of the adsorption energy, as is the steepness of the adsorption isotherm (Murali *et al*, 1983). The Langmuir adsorption isotherm was developed

by Langmuir (1918) to describe the adsorption of gases by solids. Assumption(1) leads to the concept of an upper limit of adsorption. The Freundlich isotherm does not generate any information indicating the process of adsorption is completed (Tan, 1993). However, although the Langmuir isotherm provides a useful reference standard of ideality for theoretical study, equilibria in real systems are often better represented by the Freundlich isotherm (Graham, 1959).

3.3 CHEMICAL KINETICS

The word "kinetics" is a general term, referring to time dependent phenomena. The term chemical kinetics is used to describe the quantitative study of change in concentration or pressure with time, resultant from a chemical reaction (Latham *et al*, 1977). Chemical reactions may be divided into two broad categories: homogeneous and heterogeneous. Chemists, and textbooks of chemistry, often confine themselves to homogeneous reactions, especially in the examination of chemical kinetics. In this investigation which examines the adsorption of metallic ions onto municipal solid waste, it was necessary to investigate the work of other researchers working in the similar area. An area of science where kinetic theories are adapted to the adsorption of various ions onto heterogeneous surfaces is soil chemical processes.

Since the initial development of the science of soil chemistry, attention has been given to equilibrium processes. It was only in 1989, that the first comprehensive study of time dependent soil chemical processes was promulgated by Sparks; Kinetics of soil chemical processes (Sparks, 1989). Harter (1986), a major contributor to the field of soil science, reviewed key papers in adsorption phenomena of various researchers from the 1800's to the present day. Harter thought, at that time, the state of knowledge regarding chemical kinetic studies was incomplete. The selection of papers would possibly be incautious, and instead included a bibliography of papers together with a review of recent findings and thoughts. However, with the similarities between the two areas of research, it was likely that the work of researchers in the field of soil science would be relevant.

3.3.1 Chemical interactions in soil reactions

Chemical reactions at the solid phase may comprise of: the formation or rupture of a bond between sorbate and surface; further reaction between adsorbed species; rearrangement of the solid structure and formation and disappearance of solid species. It is often incorrect to apply simple kinetic models to such interactions because reacting solid surfaces are rarely homogeneous and also the effects of transport phenomena and chemical reactions are often inseparable (Sparks, 1989). Harter (1991) notes that commonly used kinetic techniques are based on the assumption that the reactions are either unidirectional or discrete, while soil sorption reactions are often both reversible and multiple, and it is seldom possible to be definitive in calculating rate coefficients attributed to a specific reaction.

The heterogeneity of soils can be further enhanced by the variation of constituents of the soils, the differing particle sizes; types of surface sites, etc. If one considers the organic solids within soils, it is not even possible to describe a developed molecular structure for the

compounds present (Sposito, 1984). The analogy of adsorption of solutes onto soils with the adsorption of solutes onto municipal solid waste is evident. The heterogeneity of municipal solid waste regarding composition, size and size range cannot be disputed. The heterogeneity of the surface is also apparent. Therefore, conclusions regarding kinetic models for adsorption of solutes onto soils should be equally applicable for municipal solid wastes.

3.3.2 Mechanisms of soil reactions

Soil adsorption reactions may be classified as slow or rapid. Slow reactions are those in which processes taking place at the solid phase are rate determining. These processes may include: surface diffusion; diffusion within the micropores; penetration into the bulk of the solid or chemical interactions. Rapid soil reactions are, in general, reactions which transport at the solid phase does not influence the reaction rate to any significant extent (Aharoni *et al*, 1991a).

3.3.3 Application of chemical kinetics to the adsorption of metallic ions onto municipal solid waste

The application of chemical kinetics to (even) homogeneous solutions is often arduous. When kinetic theories are applied to heterogenous soil constituents, the problems and difficulties are magnified (Sparks, 1989). A similar comment could be stated for municipal solid waste surfaces, especially when those surfaces are composed of differing materials. An array of kinetic equations including zero-, first-, and second order, fractional power, Elovich, and parabolic-diffusion equations have been employed over the years to describe the kinetics of soil chemical phenomena. Kuo and Lotse (1974) successfully described the kinetics of phosphate sorption and desorption on hematite and gibbsite by the use of the fractional power or modified Freundlich equation. This equation is often termed the two-constant rate equation, and is discussed below.

3.3.4 Two-Constant Rate Equation

Kuo and Lotse (1974) developed a two-constant rate equation, adapted from the Freundlich equation by inserting a time-dependent expression into the Freundlich equation. The Freundlich equation is usually presented as shown below.

$$q = K_F C_e^M \qquad 3.1$$

The insertion of a time dependent expression results in an expression of the form,

$$q = K_a C_o t^{1/m} \qquad 3.3$$

where

Co = initial solute concentration
K_a = constant
t = time
m = constant

3.4

The two-constant rate equation was also used to describe arsenite sorption and desorption in soils (Elkhatib *et al*, 1984), potassium-calcium exchange on soils (Sparks *et al*, 1980), and by Jopony and Young (1987) to study the kinetics of copper desorption from soil and clay minerals. The modified Freundlich equation is generally considered empirical (Aharoni *et al*, 1991b).

3.3.5 Applicability of empirical equations to slow soil reactions

In many cases kinetic data experimentally obtained for activated reactions does not fit equations derived from theoretical models, but may be described by an empirical expression. These expressions, applicable to soil reactions, are also applicable to various other chemical processes involving solid-fluid reactions (Aharoni *et al*, 1991a). The three principal equations are the: modified Freundlich equation; Elovich equation; pseudo-first-order equation.

(a) Modified Freundlich or fractional power equation
Another representation of the modified Freundlich equation is;

$$q = kt^{v} \qquad 3.4$$

where

q = quantity adsorbed at time, t.
k = constant
v = constant

(b) Elovich equation
The Elovich equation is one of the most widely used equations to describe the kinetics of heterogeneous chemisorption of gases onto solid surfaces (Taylor *et al*, 1952; Low, 1960). It has subsequently been used extensively to describe the adsorption and desorption of various solutes with differing soils (Atkinson *et al*, 1970; Chien *et al*, 1980; Hodges *et al*, 1987).

The Elovich equation may be represented by;

$$q = A + (1/b)\ \ln(t + t_o) \qquad 3.5$$

where

A = constant
b = constant

The parameter t_o is often small at the range where t is applied and may often be disregarded. The applicability of the relationship may be verified by plotting q/q_∞ versus $\log_e t$. Where;

q_∞ = amount sorbed at $t = \infty$

(c) Pseudo-first-order equation
The pseudo-first-order equation may be represented by;

$$q/q_\infty = 1 - \beta \exp(-\alpha t) \qquad 3.6$$

where

β = constant

α = constant

The applicability of the relationship can be verified by plotting $\log_e(1 - q/q_\infty)$ versus t.

3.3.6 Relationship between empirical equations and diffusion

A generalised equation may be derived by closely examining the applicability of equations (3.4), (3.5) and (3.6) to experimental data (Aharoni *et al*, 1991a). These generalised expressions are obtained by differentiating the empirically based formula and writing them as the reciprocal of the rate. Consider equation (3.4)

$$q = kt^v \qquad 3.4$$

Then,

$$Z = (dq/dt)^{-1} = (1/vK)t^{1-v} \qquad 3.7$$

A similar exercise may be performed for equations (3.5) and (3.6).

Plots of the reciprocal of the adsorption rate (Z) versus time (t) for various soil reactions, and other solid-fluid processes are usually S-shaped: convex at small values of time, concave at large values of time, and linear at some intermediate value of time. It is often more convenient to plot experimental data as q (amount sorbed) versus $\log_e t$. This representation will also produce S-shaped plots. These S-shaped plots do not contradict the empirical equations whenever they are valid. The equations may be applicable, over the entire experiment, if all the points measured are within its range of validity. It should be noted however that equations (3.4) and (3.5) cannot be valid at large values of time as they give infinite sorption at infinite time. These two equations must be superseded at some time by an equation that predicts a finite saturation value at infinite time, such as equation (3.6). The generalised expression, S-shaped Z(t) plots may be explained by models based on diffusion. Equations for diffusion in a homogeneous medium lead to S-shaped Z(t) plots in which the final and initial curved parts are dominant. Equations for diffusion in a heterogeneous medium lead to S-shaped Z(t) plots in which the intermediate linear part is dominant.

3.4 NON-IDEAL REACTORS AND TRACER RESPONSE ANALYSIS

A continuous reactor may behave very much like a plug flow reactor or a perfect mixer, but it can never completely achieve either of these ideal states. In an ideal plug flow reactor, all reactant and product molecules at a given axial position move at the same rate in the direction of the bulk fluid flow, while in real flow reactors, fluid velocity profiles, turbulent mixing and molecular diffusion cause molecules to move with a variety of speeds and directions. These inevitable deviations from ideal reactor conditions lead to fundamental problems in reactor design and analysis (Dudukovic *et al*, 1983).

3.4.1 Residence Time Distribution

(adapted from Levenspiel, 1962 and Denbigh *et al*, 1971)

Consider a fluid flowing at steady state, without reaction, or density change, then,

$$\bar{t} = V/v \qquad 3.8$$

Where,

$\bar{t}$ = mean residence time (h)
V = volume (m^3)
v = volumetric flowrate (m^3h^{-1})

A dimensionless variable may be defined which measures time in units of mean residence time. This dimensionless variable is termed reduced time and is defined below.

$$\theta = t / \bar{t} = vt/V \qquad 3.9$$

Where,

θ = reduced time (dimensionless)

(a) Exit age distribution (E and E(t))

Let **E** be a measure of the distribution of ages of all elements of the fluid stream leaving the vessel. Thus, **E** is a measure of the distribution of residence times of fluid within the vessel. Then,

$\mathbf{E}\, d\theta$ = fraction of material in the exit stream between the ages θ and $\theta + d\theta$

Consider Figure 3.1, shown below

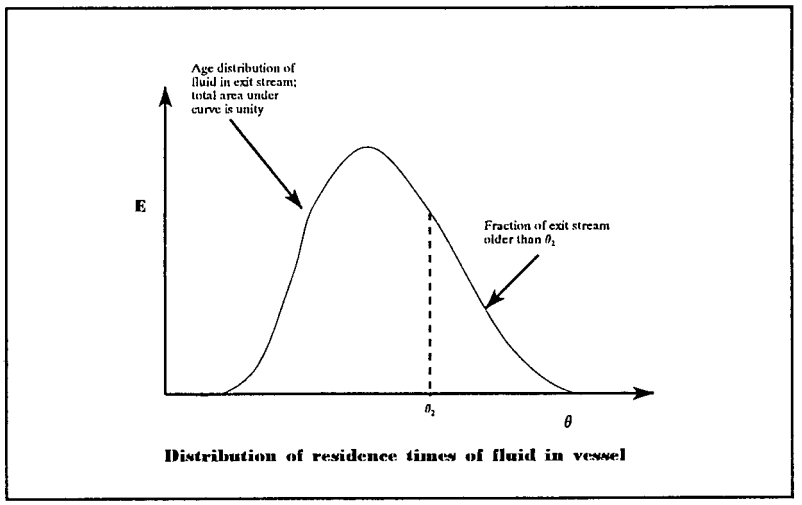

Figure 3.1
Exit age distribution or distribution of residence times of fluid in a vessel (adapted from Levenspiel, 1962)

The area under the **E** versus θ curve can be expressed

$$\int_0^\infty \mathbf{E}\, d\theta = 1 \qquad 3.10$$

The fraction of the material in the exit stream younger than age θ_2 is

$$\int_0^{\theta_2} \mathbf{E}\, d\theta$$

Then the fraction of material older than θ_2 , is defined,

$$\int_{\theta_2}^\infty \mathbf{E}\, d\theta = 1 - \int_0^{\theta_2} \mathbf{E}\, d\theta$$

Age distribution functions may be expressed in terms of real time units rather than in dimensionless time units. The exit age distribution is designated **E**(t). Now **E**(t) *d*t becomes the fraction of material in the exit stream of age between t and t + *d*t, then

$$\mathbf{E} = \bar{t}\, \mathbf{E}(t)$$

with,

$$\int_0^\infty \mathbf{E}(t)\, dt = 1 \qquad 3.11$$

also,

$$\bar{t}\theta = t$$

with

$$\bar{t} = V/v = \bar{t}_{\mathbf{E}} = \int_0^\infty t\, \mathbf{E}(t)\, dt$$

3.4.2 Experimental methods - theoretical considerations

The measurement of the exit age distribution functions cannot be made directly. An experimental method within a group of techniques classed as stimulus-response techniques must be utilised. The experimental method employed in this research, used a pulse input signal. Therefore, the subsequent discussion is limited to this approach.

(a) The C(t) curve

The curve that describes the concentration-time function of a tracer in the exit stream of a vessel in response to a pulse injection is termed here, the **C**(t) curve. Concentration and real time co-ordinates are employed. The **C**(t) curve may be related to the **E**(t) curve in the following manner.

Consider a small quantity of a suitable tracer of quantity M is introduced into the fluid entering the vessel. Consider the tracer leaving the vessel between t and t+*d*t. From the definition of **E**(t);

Quantity of tracer leaving the vessel between t and t+*d*t = M**E**(t)*d*t

Let the concentration of tracer as a function of time = **C**(t)

Also the quantity of tracer leaving the vessel between t and t+dt = **C**(t)vdt

Therefore,

$$\mathbf{E}(t) = \frac{v\mathbf{C}(t)}{M} \qquad 3.12$$

Thus, excluding the scale factor v/M, the graphical construction of **C**(t) is identical to that of **E**(t).

(b) Mean and variance of a distribution

Associated with every age distribution $y = f(x)$ are two sets of parameters called moments of the distribution. Two moments are used throughout all areas of tracer evaluation. The first moment about the origin, commonly called the mean or centroid of the distribution is the location parameter of the distribution and may be defined;

$$\mu = \int_0^\infty x\, f(x)dx \;/\; \int_0^\infty f(x)dx \qquad 3.13$$

For a continuous function measured at a number of equidistant points then

$$\mu = \Sigma\, x_i\, f(x_i)\Delta x \;/\; \Sigma\, f(x_i)\Delta x = \Sigma\, x_i\, f(x_i) \;/\; \Sigma\, f(x_i) \qquad 3.14$$

The second moment about the mean, is commonly termed the variance. The variance measures the spread of the distribution about the mean and is equivalent to the square of the radius of gyration of the distribution. It is defined for a continuous distribution as

$$\sigma^2 = \int_0^\infty (x - \mu)^2\, f(x)dx \;/\; \int_0^\infty f(x)dx \qquad 3.15$$

For a continuous function measured at a number of equidistant points then

$$\sigma^2 = \Sigma\, (x_i - \mu)^2\, f(x_i)\Delta x \;/\; \Sigma\, f(x_i)\Delta x = \left(\Sigma\, x_i^2\, f(x_i) \;/\; \Sigma\, f(x_i)\right) - \mu^2 \qquad 3.16$$

These properties may be evaluated for the **E** curve, as shown below.

The mean age of the exit stream may be defined in terms of reduced time,

$$\theta_m = \int_0^\infty \theta\, \mathbf{E}\, d\theta = \Sigma\, \theta\, \mathbf{E} \;/\; \Sigma\, \mathbf{E} = \Sigma\, \theta \mathbf{E} \Delta\theta \qquad 3.17$$

The variance of the **E** distribution may be defined,

$$\sigma^2 = \int_0^\infty (\theta - 1)^2\, \mathbf{E}\, d\theta$$

$$= \int_0^\infty \theta^2\, \mathbf{E} d\theta - 1$$

$$\sigma^2 = (\sum \theta^2 E / \sum E) - 1$$

$$= \sum \theta^2 E \Delta\theta - 1 \qquad 3.18$$

The mean age of the exit stream may be also be defined in terms of real time,

$$\bar{t} = \int_0^\infty t\,\mathbf{E}\,dt = \sum t\,\mathbf{E}(t) / \sum \mathbf{E}(t) = \sum t\mathbf{E}(t)\Delta t \qquad 3.19$$

The variance of the **E**(t) distribution may be defined,

$$\sigma_t^2 = \bar{t}\sigma^2 = \int_0^\infty (t - \bar{t})^2\,\mathbf{E}\,dt$$

$$= \int_0^\infty t^2\,\mathbf{E}(t)dt - \bar{t}^2$$

$$= (\sum t^2\,\mathbf{E}(t) / \sum \mathbf{E}(t)) - \bar{t}^2$$

$$= \sum t^2\,\mathbf{E}(t)\Delta t - \bar{t}^2 \qquad 3.20$$

3.4.3 Experimental methods - practical considerations

(a) The pulse experiment

The simplest and most direct method of evaluating the residence time distribution employs a non-reactive tracer. The method of evaluation is described below (Levenspiel, 1993). M units (mass or moles) of non-reactive tracer is introduced simultaneously into the fluid entering the vessel. The volumetric flowrate and the concentration of the tracer within that fluid is then recorded. A response curve of concentration (**C**) versus time (t) is then constructed (**C**(t) curve). The area under the curve, the mean of the curve, and the variance are then evaluated with the equations shown below.

Area under the curve $= \int_0^\infty \mathbf{C}\,dt = \sum \mathbf{C}_i\,\Delta t_i$

Mean of the curve ($\bar{t}$) $= \int_0^\infty t\,\mathbf{C}\,dt / \int_0^\infty \mathbf{C}\,dt$

$= \sum \mathbf{C}_i\,t_i\,\Delta t_i / \sum \mathbf{C}_i\,\Delta t_i$

Variance (σ_t^2) $= (\int_0^\infty t^2\,\mathbf{C}\,dt / \int_0^\infty \mathbf{C}\,dt) - \bar{t}^2$

$= (\sum \mathbf{C}_i\,t_i\,\Delta t_i / \sum \mathbf{C}_i\,\Delta t_i) - \bar{t}^2$

The calculated results are then evaluated for consistency, by use of material balance computations. The equations are shown below.

Area under the curve $= M/v$

Mean of the curve = $\bar{t}$ = V/v

From the concentration-time data the construction of the **E**(t) or **E** curve is now possible, by use of the formula shown below.

$$\mathbf{E}(t) = \mathbf{C} / \sum \mathbf{C} \Delta t$$

and,

$$\mathbf{E} = \bar{t}\mathbf{E}(t)$$

$$\theta = t / \bar{t}$$

The **E**(t)curve may be utilised to find the behaviour of the reactor directly as shown below.

3.4.4 Conversion directly from tracer information

Consider a liquid containing a solute A, that is successfully adsorbed by a suitable adsorbent. If the liquid is passed through a bed of adsorbent, initially free of the adsorbate, A, the uppermost layer of adsorbent, adsorbs the solute rapidly, subsequent layers of adsorbent remove further solute from solution until the fluid exiting the column (assuming the depth of adsorbent is sufficient) is free of solute (Treybal, 1968). These statements assume the fluid to be flowing in perfect plug flow, with the rate of adsorption of the solute to be more rapid than the vertical movement of the fluid down the column. The computation of the concentration of solute A in the exit stream in this case is relatively simple. To convert data obtained from tracer information, a sophisticated method of computation is required.

The computation to calculate the degree of adsorption of a solute employs a conventional chemical engineering mathematical approach used to solve, in the presence of unsteady state conditions. The **E**(t) curve allows the calculation of the volume of liquid leaving the column at any time increment during the total time, and hence, the velocity of that element of fluid. The calculation is then performed incrementally, in a manner similar to that of the art of screen printing (where different colours are applied at different times) for the differing residence time frames of the various elements of fluid flowing through the column. Each incremental residence time is overlaid upon the previous shorter residence times until the longest residence time is the last time frame to compute.

The increment depth of the adsorbent is firstly decided upon. In most cases, the thinner the increment of depth the greater the accuracy of the calculation. From the **E**(t) data the volume of liquid passing, over a particular time period can be computed. Therefore, the residence time of the fluid per increment of depth can be calculated. CAo is then calculated in terms of mass of solute per mass of adsorbent in the increment. It is assumed the initial solute concentration is in proportion to volume of liquid flowing in that time increment. From the kinetic expression the theoretical mass of solute to be adsorbed is calculated. This is then compared with the solute concentration within the increment. Solute may be adsorbed fully, adsorbed partially, or not at all, if the solute has already reached its equilibrium value in that increment. The concentration of solute in the fluid is reduced by the applicable amount, and this reduced fluid solute concentration then enters the next increment and the aforementioned

process begins again. This process is then repeated to the final increment of the adsorbent layer. The next element of fluid from the **E**(t) data is then manipulated in the same manner until the total residence time of all fluid elements is reached. A graphical plot of concentration of solute in the exit stream versus time may then be constructed. The computational method is shown diagrammatically in Figure 3.2

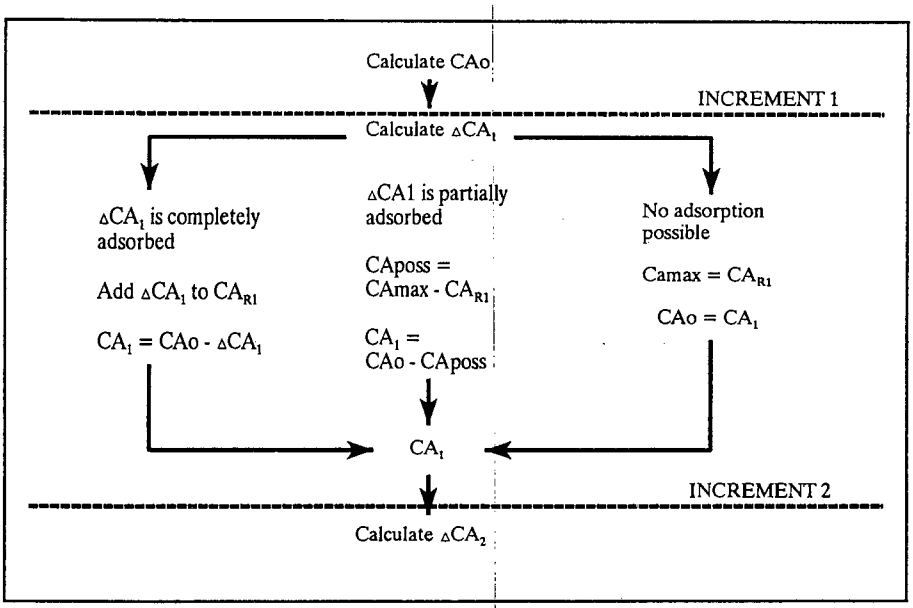

Figure 3.2
Illustration of computational method

Nomenclature

CAo	=	Solute concentration in fluid at t = 0 (gkg^{-1})
CA poss	=	Equilibrium solute concentration in adsorbent (gkg^{-1})
ΔCA_n	=	Solute adsorbed in increment n (gkg^{-1})
CA_n	=	Solute concentration in fluid entering increment n (gkg^{-1})

CHAPTER 4
EXPERIMENTAL METHODS AND PROCEDURES

4.1 INTRODUCTION

The chemical engineering principles of reactor design and transport phenomena were employed to determine the behaviour of heavy metals within the landfill environment. The metals examined were copper, chromium and arsenic, in the form of CCA (or Tanalith). This chemical is used extensively for wood preservation. The kinetics of adsorption/desorption of this substance were appraised at laboratory scale. Pilot-scale landfill columns were also constructed at Athlone, Cape Town. Tracer studies were then undertaken at pilot-scale. Tracer studies enable the deviation from ideal flow to be determined. The combination of the results from the kinetic studies and the tracer studies allow the computation of the exit stream composition. Heavy metals were then co-disposed at pilot-scale to evaluate the accuracy or otherwise of both the tracer studies and the chemical kinetics. The combination of the laboratory scale and pilot-scale studies should then allow the prediction of the amount of copper, chromium and arsenic which can be retained in a full-scale landfill operation.

4.2 EXPERIMENTAL PROCEDURE

The research into the immobilisation of copper, chromium and arsenic on stabilised domestic refuse, comprised of two complementary investigations:

4.2.1 Laboratory scale investigation

The laboratory scale investigation was also constituted of two integral sections:
(i) Evaluation of kinetic rate constants, adsorption and desorption;
(ii) evaluation of adsorption isotherms.

4.2.2 Pilot-scale investigation

This investigation advanced on two fronts:
(i) Determination of the residence time distribution/deviation from ideal behaviour of the pilot-scale landfill columns.
(ii) Evaluation, at pilot-scale, of the kinetic rate constants determined at laboratory scale.

There are elements of commonality between the four subsections, one of them being the municipal solid waste used in the experiments.

4.3 MUNICIPAL SOLID WASTE

At the outset of the experimental study it was an objective to study the effect of the co-disposal of the heavy metals with methanogenic municipal solid waste. To achieve this purpose, 5 000kg of municipal solid waste deposited at Coastal Park Sanitary Landfill Site, for approximately 1 year, was excavated. By excavating previously deposited waste, it was thought the stabilisation process could be accelerated. This would allow the experimental study to proceed more rapidly, possibly partially by-passing the acetogenic phase of landfill stabilisation. This objective was not achieved. The waste excavated was virtually stabilised i.e. at the end of the methanogenic stage of landfill stabilisation. The excavated waste was probably deposited far in excess of the estimated time of 1 year. The focus of the study changed, to the examination of the effect of the co-disposal of the heavy metals with fully stabilised municipal solid waste.

After excavation, the municipal solid waste was transported to the Swartklip Pulverising Plant, where the excavated waste underwent size reduction. The waste was shredded for three main reasons:

to avoid gross liquid bypassing in the pilot-scale landfill columns;
to achieve a similar degree of compaction to that achieved at the full-scale landfill;
to obtain a similar degree of dimensional similarity between the pilot-scale columns and the full-scale operation.

4.3.1 Sampling of the municipal solid waste

Sampling of the municipal solid waste from Coastal Park Sanitary Landfill Site was given considerable thought. Municipal solid waste is complex in composition and of a non-homogeneous nature. The United States Environmental Protection Agency have compiled information regarding the sampling of solid waste, but this information was not available. In order to proceed with the investigation other avenues were explored. These are outlined below.

Initial sampling is discussed in Municipal refuse disposal (American Public Works Association, 1970). If collecting from an area in a city, it is suggested that one truckload should be adequate, the initial sample from that truck should be 225kg. The sample should then be reduced in size to less than 4cm. After size reduction, it is recommended the sample size be reduced by quartering to approximately 4 samples, each of 100g. Moisture analysis is then performed in quadruplicate, the four samples are then reconstituted, for further analyses.

Ham and fellow researchers (1993) characterised landfill refuse from Fresh Kills Landfill on Staten Island, New York. Landfilling at Fresh Kills commenced in 1948, and is today, the largest solid waste disposal site in the world. It covers 12 000 hectares, and receives 15 500 tonnes of waste per day. The researchers drilled 13 boreholes. Several hundred kilograms of solid waste was sampled, in 100kg increments. These samples were then reduced in mass to 25kg. The method of size reduction was not discussed in detail. However, as the placing of the sample on a large sheet of plywood is mentioned, it would appear the samples were

quartered. A total of 31 samples of municipal solid waste were collected in this manner. Each increment was individually reduced in size to approximately 1.9cm. Each increment, of the now shredded municipal solid waste, was then mixed thoroughly and half of each individual increment discarded. Finally, the remaining 12.5kg of shredded solid waste was separated by riffling into 16 approximately 0.75kg increments. Five (5) of these sub-samples were used for replicate analysis. In some instances, these 5 sub-samples were combined in equal amounts for analysis.

Klee and Carruth (1970) investigated sample weights in solid waste composition studies. Both researchers were employed at that time by the United States Bureau of Solid Waste Management and had access to studies conducted by the Bureau. They examined samples taken at nine different incinerator sites. Samples taken at the sites were varied in three different mass ranges, the largest sample being approximately 750kg, the smallest being 90kg. The researchers found no significant differences with regard to precision for the studied sample mass groups of 75kg to those of greater mass. It should be noted there was no significant difference between the mass of waste divided into 9 subgroups such as food wastes, garden waste, etc. The researchers concluded it was not advantageous to take samples of mass greater than 75kg, to analyse any given waste stream.

Musa and Ho (1981) also investigated the optimum sample size for solid waste analysis. Initially, they examined the work of other researchers and organisations. They cite the United Kingdom's Institute of Public Cleansing who advised in 1964, a sample be taken of not less than 1 tonne, in total mass, from not less than 100 premises. They examined the results of four waste surveys undertaken in Australia. Unfortunately, the researchers were primarily interested in household waste surveys. However, one important result of their studies was, their results indicated the number of increments taken was of greater importance, with regard to accuracy of results, than the total mass of the sample.

The **A**merican **S**ociety for **T**esting **M**aterials (ASTM) practices for sampling various solid materials including solid waste, were also examined. Those standards examined included:

Standard Practice for Sampling Aggregates Designation: D75 - 87 (Reapproved 1992)

Standard Test Methods for Collection of a Gross Sample of Coal Designation: D2234 - 89

Standard Test Method for Determination of the Composition of Unprocessed Municipal Solid Waste Designation: D5231 - 92

When sampling aggregates, the larger the nominal size of the aggregate, the larger the minimum sample size. For coarse aggregate of size 90mm, coupled with sampling from a stockpile (an unsatisfactory sampling situation), a minimum of 3 increments is recommended of minimum mass per increment, 55kg. The sampling of raw or uncleaned coal was also examined. It is recommended, for uncleaned coals above 150mm in size, the minimum number of increments be 35, of minimum mass 7kg. This method would be statistically correct, for a total mass of raw coal not exceeding 900 tonnes. The ASTM method for sampling unprocessed municipal waste is based on classification sampling (allowing categorisation of waste sampled; paper, plastic, etc.). It is recommended a sample size of 91 - 136kg would be representative of a vehicle load of municipal solid waste.

All of the above were considered to ensure representative sampling of the excavated municipal solid waste. Key points noted were: the correct sample size should approximate 75kg (Klee *et al*, 1970); the correct sample size should approximate 225kg (American Public Works Association, 1970); the greater the number of increments the greater the degree of accuracy that can be expected (Musa *et al*, 1981); when sampling uncleaned coal above 150mm in size, of total mass 900 tonnes, the minimum number of increments be 35, of minimum mass 7kg (ASTM, 1993).

The total mass of excavated municipal solid waste from Coastal Park Sanitary Landfill approximated 5 000kg. The solid waste was sampled after size reduction, prior to transportation to the pilot-scale landfill columns. Reduction of size before sampling is advantageous, as the homogeneity of the solid waste is improved. As the solid waste was loaded for transportation, incremental sampling was practised at equally spaced time and mass intervals. A total of 20 increments were taken, the average weight of each increment being approximately 11kg. Therefore, the total mass of the sample of municipal solid waste was 230kg. This method of sampling should eliminate any sources of error and ensure samples taken for use in the laboratory were fully representative of that municipal solid waste loaded into the pilot-scale landfill columns.

After sampling, the incremental samples were placed in thick plastic bags, sealed with nylon cord. These plastic bags were then subsequently placed in another plastic bag, the outer plastic bag being sealed in an similar manner. This method was utilised to ensure that any moisture associated with the municipal solid waste was not lost, as the first step in the sample preparation was determination of moisture content.

4.3.2 Sample preparation: municipal solid waste

On arrival at the laboratory, each incremental sample was opened individually and the municipal solid waste placed onto a clean, dry, concrete area. Each increment was then mixed rapidly, cut into quarters, a shovel full taken from each quadrant until it was judged sufficient mass, in this case approximately 5kg was available for the determination of moisture content. The remainder of the increment being labelled, re-bagged and stored. The municipal solid waste for moisture determination was then placed within the drying oven. The sample was then dried at 75°C for 48 hours (American Public Works Association, 1970). It was then removed from the oven and allowed to cool, and weighted, the weight being noted. The incremental sample was then replaced within the oven for a further 24 hours. The sample was then removed from the oven, allowed to cool and reweighed. If no further weight change was evident, the sample was made available for size reduction. The results of moisture determination are shown overleaf in Table 4.1.

Table 4.1 Moisture content of municipal solid waste from Coastal Park Sanitary Landfill Site

Sample No.	Initial increment mass (kg)	Mass of sample to be dried (g)	Mass of dried sample (g)	Percent moisture (dry)	Percent moisture (wet)
1	9.0	3720.1	2893.6	28.6	22.2
2	8.5	4156.3	3209.8	29.5	22.8
3	12.5	6235.5	4979.4	25.2	20.1
4	23.3	5425.6	4282.7	26.7	21.1
5	10.5	4506.4	3640.7	23.8	19.2
6	10.5	5012.1	3963.7	26.5	20.9
7	10.6	5516.6	4396.3	25.5	20.3
8	10.1	5397.0	4296.0	25.6	20.4
9	9.2	4452.7	3598.3	23.7	19.2
10	10.8	4381.7	3529	24.2	19.5
11	9.3	4634.7	3709.8	24.9	20.0
12	8.5	3993.5	3246.3	23.0	18.7
13	12.6	5417.5	4324.1	25.3	20.2
14	14.3	5688.2	4626.4	23.0	18.7
15	9.7	5271.8	4238.7	24.4	19.6
16	13.6	6047.8	4726.8	27.9	21.8
17	14.7	5667.8	4469.0	26.8	21.2
18	8.3	3896.3	3024.3	28.8	22.4
19	10.6	4805.3	3898.4	23.3	18.9
20	12.7	6910	5424.5	27.4	21.5
Average				25.7	20.4

After moisture determination, the incremental samples were then individually reduced in size to approximately $5cm^2$ by use of hand scissors and tin snips. It is advised by the American Public Works Association's Tentative methods of analysis of refuse and compost (American

Public Works Association, 1970) to discard inorganic materials such as glass, metals and ceramics. In South Africa, with the extremely efficient scavenging of waste (indicative of it's socio-economical problems) at landfills, and prior to disposal, there was a marked absence of commodities of this nature. After the first stage of size reduction, the incremental sample was then reduced in mass by the method previously described to approximately 2kg. The remainder of the increment being labelled, re-bagged and stored. The incremental sample, of mass 2kg, was then further reduced in size with a laboratory electrically driven hammer mill, to pass through a 1mm sieve.

This degree of size reduction conforms with the size range specified by the United States Environmental Protection Agency Method 1311 Toxicity Characteristic Leaching Procedure (US EPA Method 1311 TCLP) (US EPA, 1992). It is a requirement of the US EPA the solid waste must pass through a 9.5mm standard sieve. The Public Works Association's Tentative methods of analysis of refuse and compost (American Public Works Association, 1970), require the waste to be ground to pass through a 1mm sieve. There is not mention of a minimum size, in the documentation supplied by the US EPA. After final size reduction, each sample increment was placed in a 2ℓ plastic bucket fitted with a snap-fit plastic lid. Prior to storage, each increment was well mixed, and a small amount, approximately 200g, was removed from each increment and placed in an additional pail. This increment was labelled sample 21 and was deemed fully representative of the solid waste previously placed in the pilot-scale landfill columns. The characterisation of the municipal solid waste is shown in section 4.3.3, Tables 4.2 and 4.3.

4.3.3 Characterisation of the municipal solid waste

(a) Metal content

Table 4.2 Metal content: municipal solid waste sampled at Coastal Park Sanitary Landfill Site

Sample No.	Copper	Chromium	Zinc	Cadmium	Nickel	Lead	Potassium	Phosphorous
3	28	37	345	1.3	6	142	1047	5.4
6	22	11	116	1.3	11	46	823	106
9	15	5	135	1.5	9	32	1249	5.7
12	18	8	127	0.8	35	48	621	2.4
15	34	16	212	1.7	15	143	1261	5.5
18	31	21	309	1.4	4	60	1195	193
Average	25	16	207	1.3	13	79	1033	53
21	29	12	265	0.8	17	45	1240	32

All results quoted above in ppm (w/w). Sample No. 21 is the cumulative sample, of all the incremental samples taken.

(b) Additional analyses

Table 4.3 Additional analyses: municipal solid waste sampled at Coastal Park Sanitary Landfill Site

Sample No.	pH	Volatile solids (percent)	Total Kejldahl Nitrogen ($mg\ell^{-1}$ N)
3	7.7	32.6	20
6	8.0	19.2	10
9	7.8	23.5	40
12	7.7	16.4	20
15	8.2	24.9	10
18	8.4	27.6	10
Average	8.0	24.0	20
21	8.1	17.4	20

ENCON Associates conducted a field scale landfill project at the Mountain View Landfill, in California (Pacey, 1989). The researchers examined the process of methane gas generation in municipal solid waste landfills, and evaluated the effectiveness of different methods used to enhance methane generation. Six large test cells were constructed each containing approximately 7 500 tonnes of municipal solid waste. The cells were treated with differing stabilisation enhancement techniques, one cell remained untouched, and was used as a control. After five years, the cells were subjected to rigorous municipal solid waste sampling. Additionally, adjacent solid waste was sampled. They examined 28 samples, with 5 replicate analyses per sample. The only heavy metal identified for analysis was nickel. Nickel has been identified as possibly inhibitive in the landfill environment. It is of interest to examine the results from the control cell, and that of adjacent refuse, and compare these with the results of municipal solid waste excavated from Coastal Park Sanitary Landfill Site which was estimated to be of age 1 year. Details of the municipal solid waste excavated from Mountain View and Coastal Park Sanitary Landfill Sites are shown below in Table 4.4.

Table 4.4 Characterisation of municipal solid waste: Mountain View and Coastal Park

Component	Mountain View (control cell)	Mountain View (adjacent municipal solid waste)	Coastal Park (average values)
Moisture content (%)	40.0	22.0	20.4
pH	6.7	6.8	8.0
Volatile solids (%)	43.5	27.1	24.0
Kjeldahl Nitrogen (ppm [w/w])	0.4	0.3	20
Phosphorous (ppm [w/w])	279	185	53
Nickel (ppm [w/w])	6.3	3.7	13

It is difficult to compare results because of the variable composition of municipal solid wastes as received at landfill sites in different countries. However, the low percentage of volatile solids in the municipal solid waste excavated from Coastal Park Landfill Site is probably indicative that the solid waste was actually in excess of 1 year of age. The percentage volatile solids of the solid waste excavated from Coastal Park Sanitary Landfill site averaged 24 percent. The solid waste excavated from Mountain View Landfill was 43.5 percent in the control cell and 27 percent in the adjacent solid waste, after being deposited for 5 years.

4.4 COPPER-CHROMIUM-ARSENIC WOOD PRESERVATIVE

4.4.1 Characterisation of the copper-chromium-arsenic wood preservative

The copper-chromium-arsenic product employed in this investigation is marketed by Rentokil South Africa (Pty) Ltd., it is designated *Celcure A Paste*. The specification as supplied on the product is as shown overleaf:

Copper:	71g per kg
Chromium:	119g per kg
Arsenic:	128g per kg

The relative density of the solution is quoted as 1.85.

The method of data presentation employed by Rentokil South Africa (Pty) Ltd., tends to obscure the actual composition of the product. The composition as stated in the Material Safety Data Sheet is as shown below (Rentokil South Africa, 1994):

Component	Percent weight by weight
Arsenic pentoxide	24.63
Sodium dichromate	38.25
Copper sulphate	30.42

Analysis in the laboratory revealed the following mixture of the following composition:

Component	Grams per litre
Arsenic (as As)	270.2
Chromium (as Cr)	269.6
Copper (as Cu)	93.1

The solution was also analysed to determine speciation of the chromium and arsenic. Analysis revealed the chromium to be composed of 94.8 percent chromium(VI); the arsenic was composed of 97.1 percent arsenic(V). The European Economic Community Classification is Corrosive (Harmful); the Hazard Symbol employed is "Corrosive".

4.5 EVALUATION OF THE KINETICS OF ADSORPTION OF COPPER, CHROMIUM AND ARSENIC AT LABORATORY SCALE

The kinetics of adsorption of the solution of copper, chromium and arsenic was examined by modifying the US EPA Method 1311 **T**oxicity **C**haracteristic **L**eaching **P**rocedure (TCLP). The procedure is described in detail in Appendix A.

4.5.1 Modification of the Environmental Protection Agency Method 1311 Toxicity Characteristic Leaching Procedure: kinetics of adsorption

The TCLP was modified to enable the determination of the degree of adsorption, and the rate of that adsorption of industrial waste onto municipal solid waste. The extraction fluid used is composed of glacial acetic acid, sodium hydroxide and deionised water. The composition is shown below:

Component	Percent volume
Glacial acetic acid	0.57
Sodium hydroxide	4.00
Deionised water	95.43

This solution is termed Extraction fluid #1 in Method 1311 (Appendix A). The solution's acetate buffered system would appear to provide a good approximation of leachate from a landfill in the acetogenic phase of stabilisation. The procedure for the preparation of the

extraction fluid; addition of the copper-chromium-arsenic; pH adjustment, is described in depth below. Equivalent attention to detail in chemical procedures was practised throughout. However, in the interest of brevity, the reader is referred to this section (section 4.5.1) when similar chemical procedures are discussed. The modification of the EPA TCLP was effected in the following manner. The solution was formulated as shown above. Upon formulation, the pH was determined to ensure the fluid was correctly produced. If the procedure is followed correctly, the pH of the solution should be 4.93 +/- 0.05 pH units.

The copper-chromium-arsenic solution was available in a 25ℓ container. The contents of the container was firstly well mixed. From that container, an aliquot of volume 2.5ℓ was taken and placed in a glass winchester bottle. This bottle was subsequently used in all ensuing experiments. From this container, after ensuring the contents were well mixed, 10mℓ of the concentrated copper-chromium-arsenic solution was then transferred by pipette into a 100mℓ volumetric flask, deionised water was then added to the volumetric flask to the prescribed point. The reason for this exercise being, the copper-chromium-arsenic solution is viscous, dilution was necessary to maintain accuracy. Approximately 500mℓ of the extraction fluid was then transferred into a 2ℓ glass measuring cylinder, to this was added 10mℓ of the diluted copper-chromium-arsenic solution, the solution was then mixed with a glass rod. Further extraction fluid was then added to glass measuring cylinder until the solution was 1ℓ in volume. The solution was again stirred to assure uniformity. It had been previously calculated that this degree of dilution would provide a solution of composition:

copper, approximately 80mg;
chromium, approximately 260mg;
arsenic, approximately 260mg.

It is a requirement, when conducting adsorption studies, that sufficient heavy metals are available at the start of the study to ensure an excess of metal in solution, at completion of the experiment.

A sample of volume 25mℓ was then taken. The pH of the solution was then measured. The pH of the solution was then adjusted with a 1N sodium hydroxide until the desired pH was achieved. Three pH values were chosen, pH5.5; pH6.4; and pH7.0. These pH values were selected as these values cover the usual range of pH encountered in full scale landfill operations. The measuring cylinder was then placed on the laboratory bench for approximately 30 minutes. This allowed any precipitation of the metals in solution to occur. After precipitation had occurred, the supernatant was then transferred into another measuring cylinder. A 25mℓ sample was then taken for analysis.

All 21 samples of the prepared municipal solid waste were available in the laboratory. To assure the results of the kinetic studies to be reproducible, and to eliminate any bias from the municipal solid waste, it was decided to perform the experiments in triplicate, at the three pH values. Another provision was made to assure reproducibility; at the three pH values one sample of the cumulative sample (sample 21) was used, the other two samples being differing sub-samples. This was done at every stage of the laboratory investigation.

A 50g portion of the prepared municipal solid waste was weighted and placed in the extractor vessel. The extractor vessel employed was a 2ℓ Schott bottle, fitted with a screw neck, with an internal teflon seal, within the plastic screw top. Exactly 1ℓ of the relevant pH-adjusted, dilute copper-chromium-arsenic solution was then added to the extractor vessel. The extractor vessel was then placed in the agitation device and agitation began. Samples of the dilute copper-chromium-arsenic solution, of volume 25mℓ, were then taken at designated time intervals throughout the duration of the experiment. These samples were taken at time zero, then subsequently after 0.5h, 1.0h, 2.0h, 4.0h, 8.0h, 16.0h, and 32.0h. From the examination of adsorption studies conducted by soil scientists examining the adsorption of various metals onto soils, it was thought an total experimental duration of 32 hours would be adequate. To confirm this, an initial trial was undertaken. After completion of the experiment the pH of the solution in the extractor vessel was determined.

The pH of the solutions was elevated during the experimental procedure. This elevation of pH is discussed in Section 6.7. The initial and final values of solution pH are shown below in Table 4.5.

Table 4.5 Change in pH during experimental procedure

Coding	Initial pH	Final pH
A	5.5	7.0
B	5.5	7.0
C	5.5	7.0
D	6.4	8.0
E	6.4	8.0
F	6.4	8.0
G	7.0	8.2
H	7.0	8.6
I	7.0	8.1

4.5.2 Modification of the Environmental Protection Agency Method 1311 Toxicity Characteristic Leaching Procedure: kinetics of desorption

On completion of the adsorption procedure, the contents of each extractor vessel were then filtered. Deionised water was added to the extractor vessel to ensure all solid particles were removed from the vessel, onto the filter paper. The filter paper plus solids was then

removed from the Buchner funnel and placed in a stainless steel tray. The tray was then placed into a drying oven adjusted to a temperature of 50°C. The trays remained in the oven until all traces of moisture were removed.

The dried solids were then transferred into the extractor vessel. Approximately, 1ℓ of the relevant pH-adjusted extraction fluid was then prepared. A small aliquot was then taken for analysis, and exactly 1ℓ of the extraction fluid was added to the extractor vessel (a sample subjected to adsorption at a particular pH value was desorbed at the same pH value). The extractor vessel was then placed in the agitation device and agitation began. Samples of the extraction fluid of volume 25mℓ, were then taken at designated time intervals. Samples were taken at time zero, then subsequently after 0.5h, 1.0h, 2.0h, 4.0h, 8.0h, 16.0h, and 32.0h. On completion of the experiment the samples were preserved by the addition of the relevant quantity of 10M nitric acid (Standard Methods, 1992).

4.6 LABORATORY SCALE EVALUATION OF ADSORPTION ISOTHERMS

The kinetic studies commenced with initial concentrations of copper, chromium and arsenic of approximately, 80; 260; and 260mgℓ^{-1}, respectively. To construct adsorption isotherms, additional data at lower concentrations is a requirement.

A similar procedure was then undertaken to that described previously in the evaluation of adsorption kinetic rate constants (section 4.5.1). Again, three pH values were chosen, pH5.5; pH6.4; pH7.0. Differing amounts of the diluted copper-chromium-arsenic solution were then added to the pH adjusted extraction fluid. The concentration range was:

Copper (mgℓ^{-1})	80	50	40	15
Chromium (mgℓ^{-1})	260	180	130	50
Arsenic (mgℓ^{-1})	260	180	130	50

The samples taken during the evaluation of the kinetic rate constants for the adsorption of the various metals onto the municipal solid waste had already been analysed and the results partially evaluated. There did not appear to be any difference in the adsorption/desorption characteristics displayed by the various sub-samples of the municipal solid waste. However, it was decided to be prudent and to vary the sub-samples again. All 21 samples of the municipal solid waste were available in the laboratory. The cumulative sample (sample 21) was employed at each varying concentration of the copper-chromium-arsenic solution, the remaining two samples being differing subsamples from those employed in the kinetics investigation. Samples of the dilute copper-chromium-arsenic solution, of volume 25mℓ, were then taken prior to the commencement of agitation. A final 25mℓ sample of the solution was then taken for analysis after 32 hours had elapsed. On completion of the experiment, all samples were then preserved by the addition of the relevant quantity of 10M nitric acid (Standard Methods, 1992).

4.7 PILOT-SCALE INVESTIGATION

Pilot-scale landfills have been utilised to observe and quantify phenomena occurring in landfills for over twenty five years. Many different types of experiments have been conducted, and their use is well documented.

4.7.1 Design and construction of the Athlone pilot-scale landfill columns

The initial step in the design of the pilot-scale landfill columns was to survey the literature and to review the constructional techniques employed by previous researchers. These are summarised in tabular form below. In evaluating the designs tabulated, one can observe a gradual simplification of the design of the pilot-scale columns, with the design Pohland pioneered (Pohland, 1975), becoming virtually a standard. The design of the University of Cape Town pilot-scale columns was very similar to the column that originated in Atlanta, at the Georgia Institute of Technology, designed by Pohland.

Table 4.6 Design aspects of pilot-scale landfill columns: I

Researchers	Number of columns	Height of columns (m)	Cross-sectional Area (m^2)	Configuration	Material of construction
Qasim & Burchinal (1970a, 1970b)	4	1.2, 2.4, 3.6, & 4.8	0.6362	Circular	Concrete
Fungaroli & Steiner (1971)	1	3.96	1.83	Square	Low carbon steel coated with fibreglass
Rovers & Farquhar (1973)	3	4.3	2.545	Circular	
Pohland (1975)	4	-	0.65	Circular	Steel
Newton (1977)	-		5.0	Rectangular	Concrete internally coated with epoxy
DeWalle *et al* (1978)	18	0.75	0.255	Circular	Steel walls with plastic liner
Raveh & Avnimelch (1979)	16	2.5		Circular	Poly Vinyl Chloride
Pohland (1980)	2	5.2	9.0	Square	Reinforced concrete coated with sealant
Tittlebaum (1982)	4	3.4	0.7854	Circular	Epoxy coated corrugated steel pipe

Table 4.6 Design aspects of pilot-scale landfill columns: I (continued)

Researchers	Number of columns	Height of columns (m)	Cross-sectional Area (m^2)	Configuration	Material of construction
Ham & Bookter (1982)	8	1.5	165.62	Rectangular	One wooden wall, three concrete walls
Collins & Spillman (1982)	8	5.0 to 6.0	19.64	Circular	Poly ethylene flexible walls
Pohland *et al* (1985, 1986a)	4	4.27	0.65	Circular	Corrugated steel pipe
Gould *et al* (1989)	10	4.27	0.65	Circular	Steel
Reinhart & Pohland (1991)	2	3.0	0.65	Circular	Steel
Pohland (1992)	5				
Pohland *et al* (1993)	3	3.25	0.65	Circular	Steel
Otieno (1994)	4	-	0.159	Circular	
Chapman & Ekama (1991); Novella *et al* (1996)	6	4.25	0.283	Circular	Galvanised steel coated with epoxy

Table 4.7 Design aspects of pilot-scale landfill columns: II

Researchers	Underdrain	Distributor	Instrumentation	Environment	Insulation
Qasim & Burchinal (1970a, 1970b)	Size graded clinker,(8 - 13cm) 20mm steel outlet pipe	-	Thermocouples	Outdoor	None
Fungaroli & Steiner (1971)	Sand & glass beads	Perforated plastic pipe	Thermocouples	Indoor	Insul-ation plus heating tapes
Rovers & Farquhar (1973)		Perforated tubing	Thermocouples	Outdoor & Indoor	Indoor cell, Insulated
Pohland (1975)		Positioned in soil top cover			
Newton (1977)	-			Outdoor	
DeWalle *et al* (1978)	Gravel (15cm)	Sprinkler	Thermocouples	Indoor	None
Raveh & Avnimelch (1979)	Glass beads	0.3m sand		Indoor	None
Pohland (1980)		Positioned in gravel between MSW & top cover		Outdoor	Styro-foam
Tittlebaum (1982)	0.3m of sand	PVC pipe placed in sand layer		Indoor	None
Ham & Bookter (1982)		None	Thermocouples	Outdoor	None

Table 4.7 Design aspects of pilot-scale landfill columns: II (continued)

Researchers	Underdrain	Distributor	Instrumentation	Environment	Insulation
Collins & Spillman (1982)			Thermocouples	Outdoor	
Pøhland *et al* (1985, 1986a)	Graded aggregate	Placed in aggregate layer between topsoil and MSW		Outdoor	None
Gould *et al* (1989)	Graded aggregate	Placed in aggregate layer between topsoil and MSW		Outdoor	None
Reinhart & Pohland (1991)				Indoor	
Pohland (1992)					
Pohland *et al* (1993)	Soil		Thermocouple		
Otieno (1994)	Gravel (100mm) placed on grate	Placed in 200mm gravel top layer		Indoor	None
Chapman & Ekama (1991): Novella *et al* (1996)	Graded pebbles, 20mm steel pipe	Perforated tubing	Thermocouple	Outdoor	40mm glass fibre

A diagram of the pilot-scale landfill columns constructed at Athlone is shown overleaf. Subsequently, the principal design considerations are discussed.

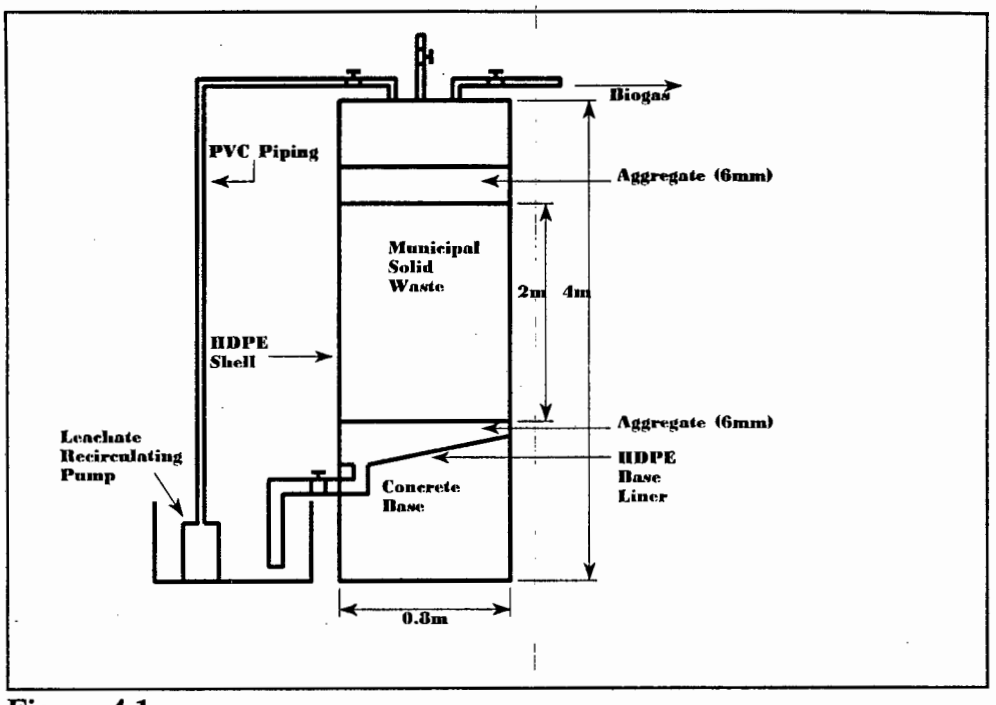

Figure 4.1
Diagrammatic representation of the Athlone pilot-scale landfill columns

(a) Column Shell

Problems had been experienced with the previous columns at the University of Cape Town. Attention had been paid to the durability of the columns, the 2mm gauge steel had been hot-dipped galvanised prior to an internal coating of epoxy paint. Corrosion problems occurred and Novella (1996) had difficulty in the latter stages of his experimental programme preserving the integrity of the columns.

The envisaged material should be inert to the products of decomposition of the municipal solid waste, such as the low pH leachate experienced; able to withstand the elements, as it was envisaged the pilot-scale columns would be outdoor; mechanically strong enough to hold the municipal solid waste. It was extremely important that chemical wall effects be avoided. A plastic type material was considered to be one of the better options available. Tittlebaum (1982) had successfully constructed a pilot-scale landfill column shell from polyvinylchloride.

Scrap **H**igh **D**ensity **P**oly **E**thylene (HDPE) pipe became available from the City Engineers Department of the City of Cape Town. The dimensions of this pipe were, internal diameter 0.70m, external diameter 0.80m, the pipe was available in varying lengths. It was decided that five columns would be sufficient to meet the aims and objectives of the project. The pipes were firstly cut to a length of 4.1m.

(b) Underdrain

The next step in the design of the pilot-scale landfill columns was to determine the underdrain design. Again, the design of previous columns were surveyed. It was decided

to cut the columns near to the base at an angle near to the base of the column, seal the base of the column with a HDPE plate, and to use a layer of 6mm aggregate as the underdrain.

(c) Column shell construction

The pipe was then cut 1m from the base at an angle approximating 30 degrees to the horizontal plane. The 0.8m base was then secured to a concrete plinth by means of steel tie-rods, the base being partially filled with concrete. A square notch was then cut into the HDPE base at the lowest point of the 30 degree cut. Shuttering was then placed around the notch and the remaining space within the base filled with concrete.

The longer of the two lengths of HDPE pipe was then sealed with an elliptical plate of HDPE. Prior to sealing a 50mm hole was drilled in the sheeting at what was anticipated to be the lowest point of the column. A short stub of 50mm polyvinylchloride pipe was securely fixed into the hole, by means of a plastic securing lock-nut either side of the plate. An articulated crane lifted the 3.2m length of HDPE piping into the vertical position; the pipe was then lowered onto the base. The upper section was secured to the base by means of a steel collar, the column was further secured to the external wall of a single storey building located behind the column. On completion of the erection of the column shell, a 50mm polyvinyl chloride ball valve was affixed to the 50mm stub, leading to a U-bend, on the outside of the column. A plastic grid was then glued to the stub in the inside of the column. The columns were then filled completely with water to test their integrity.

(d) Distributor

Again the design of previous columns was examined, it was considered earlier designs could be simplified further. It was thought, if one placed a layer of aggregate of sufficient depth above the municipal solid waste within the column, adequate dispersion of any liquid added would occur before contact with the solid waste. A layer of 6mm aggregate of thickness 45cm would be sufficient.

(e) Associated pipework and tankage

As mentioned, it was decided to use 50mm diameter polyvinylchloride pipe as the outlet pipe from the base of the column. This relatively large diameter pipe was used to discourage any blockages. To enhance landfill stabilisation, leachate recirculation is necessary. This was provided by placing a 80ℓ vessel at the base of the column. Within the vessel was placed a small submersible pump. All other associated pipework was 25mm diameter polyvinylchloride.

(f) Instrumentation

The design of previous columns was examined. Early columns were often fitted with a number of thermocouples, usually positioned with varying depth. Fugaroli and Steiner (1971) placed 4 thermocouples in a column containing solid waste of height 2.4m, while DeWalle and co-workers (1978) placed 3 thermocouples in a column containing solid waste of height 0.6m. Later columns were usually only constructed with one thermocouple in position (Chapman *et al*, 1991; Pohland *et al*, 1993). The Athlone pilot-scale columns employed one thermocouple per column, the thermocouple being positioned centrally in the solid waste.

(g) Insulation

The wall thickness of the column shell is 50mm, the material of construction being HDPE, a material of low thermal conductivity. It was considered that in the Cape Town, with its Mediterranean climate, insulation was not required. The HDPE column shell was black in colour. When the columns were first erected it was mid-Summer, it was noticed that the outer skin temperature became relatively hot. Before the municipal solid waste was placed in the columns the outer column shell was painted white. This immediately alleviated the problem.

(h) Municipal Solid Waste

For the purposes of our investigation, the height of municipal solid waste in the column was to be 2m. This height was dictated by prevailing conditions used by the City of Cape Town in their full scale landfill operations. The landfill sites within the municipality are operated such that there is a 2m layer of waste, soil cover, another 2m layer of waste, soil cover, and so on. This also conformed to the configuration used by other researchers in the field. The solid waste was reduced in size to between 25-40mm before introduction into the column. Again, this conformed to methods pioneered by other researchers. The bulk density of the municipal solid waste at the full scale landfills in Cape Town approximates $1000kgm^{-3}$. To model the full scale landfill at pilot-scale it is desirable to achieve densities of that order. Both Newton (1977) and Pohland (1975) were censured by Cope (1983) regarding the density of the municipal solid waste in their work. The average bulk density of the municipal solid waste in the pilot-scale landfill columns was $922kgm^{-3}$.

After the 6mm aggregate drainer was placed in the column shell; the column was drained after hydraulic testing; the column was then measured internally and marked at a distance exactly 2m from the top of the underdrain. The shredded municipal solid waste was incrementally weighted prior to placing in the columns The pulverised solid waste was then periodically compressed by hand to ensure the correct densities were achieved. The results are shown below in Table 4.8.

Table 4.8 Pilot-scale landfill columns: physical characteristics of the municipal solid waste

Column	Internal diameter (m)	Height of MSW (m)	Mass of MSW (kg)	Volume (m^3)	Density (kgm^{-3})
1	0.7	1.88	694	0.7235	959
2	0.7	1.94	669	0.7466	896
3	0.7	1.94	668	0.7466	895
4	0.7	1.94	676	0.7389	915
5	0.7	1.94	694	0.7351	944
Average					922

4.7.2 Operation of the pilot-scale landfill columns

In this section, the general operation will be discussed initially. Subsequently, detailed consideration will be given to the different aspects of the monitoring.

The operation and monitoring of the column temperatures commenced on Wednesday, February 8th, 1995; designated Day Zero (0). Soon thereafter, on Day 12, water was added to the pilot-scale columns, to bring the municipal solid waste to field capacity. Water was added at a rate of 30ℓ per day over a period of 5 days; Day 12, Day 13, Day 14, Day 15 and Day 16. A total of 150ℓ was added. There was no further addition of moisture for a period of one month. The temperature of the columns continued to be monitored daily, and every 7 days the outlet of the pilot-scale landfill was opened and examined for leachate. No excess moisture was found during this period. Addition of water again commenced on Day 44. Water was added at a rate of 30ℓ per day over a period of 5 days; Day 44; Day 45; Day 46; Day 47; Day 48; a total of 150ℓ was added, the total volume of water added to the pilot-scale columns now being 300ℓ.

After the addition of the additional water, monitoring the columns for biogas commenced. Monitoring of the pilot-scale landfills every 7 days continued. The next occasion the outlets were examined (after the second addition of water), no leachate was present. Leachate was present when the column drains were examined on Day 60. The columns were then drained until the flow of leachate ceased. The volume of leachate was measured, and a sample of leachate taken for analysis. The leachate was then pumped back to the top of the column and added to the municipal solid waste, to enhance the stabilisation process. The initial draining of the columns provided a relatively large quantity of leachate. With the second draining and subsequent recirculation the quantity of leachate was reduced substantially. This value is used in the table below showing the field capacity of the municipal solid waste in the column. The volume of leachate drained

is deducted from that added. Probably, the initial relatively large quantity of leachate drained from the columns was caused by a mixture of liquid by-passing and wall effects. The physical characteristics of the municipal solid waste *in situ* in the columns is shown in Table 4.9

Table 4.9 Pilot-scale landfill columns: field capacity of the municipal solid waste

Column	Initial total mass (kg)	Initial mass of water present (kg)	Initial mass of bone dry MSW (kg)	Water added - Leachate drained (kg)	Total mass of water Day 67 (1995-03-16)	Percent moisture content (wet)
1	694	142	552	267	409	41.8
2	669	136	533	260	396	42.6
3	668	136	532	247	383	41.9
4	676	138	538	263	401	42.7
5	694	142	552	256	398	41.9
Average						42.2

(a) Leachate recirculation

Leachate first became evident on Day 60. The following procedure was then followed. Leachate was drained until the flow diminished to a slow drip. While the leachate was flowing a sample was taken for analysis. On these samples the following analyses were performed:

pH;
Electrical conductivity;
Chemical **O**xygen **D**emand (COD), unfiltered;
Chemical **O**xygen **D**emand (COD), filtered;
Chloride content;
Total Alkalinity;
Bicarbonate Alkalinity;
Orthophosphate.

From the analyses of total alkalinity, bicarbonate alkalinity and orthophosphate, the volatile acid alkalinity was then calculated.

After the leachate flow diminished to a slow drip, the outlet valve from the pilot-scale column was then closed and the volume of leachate drained was measured. This was accomplished with a calibrated dip stick. The leachate was then pumped to the top of the

column by means of the permanently located submersible pump. The recirculation procedure was performed every 7 days, until Day 118. Recirculation was ceased at this point as the temperature inside the columns had dropped to below 15°C and there was no evidence of biogas production. The lower temperatures were due to the onset of the South African winter season.

Recirculation of leachate recommenced on Day 231, ambient temperatures were beginning to rise, as the southern hemisphere summer season was beginning. The recirculation procedure then continued as before the procedure being repeated after a time interval of 7 days. The procedure ceased on Day 358, as there was no resumption of biogas production.

(b) Volumetric biogas monitoring

Volumetric biogas monitoring commenced Day 54 prior to the addition of water, on Day 60. The instrument employed was a wet type gas flow meter manufacturer by Alexander Wright & Company (Westminster) Limited, model DM3A. One gas meter was used to monitor all 5 columns. The mode of operation is outlined below.

The meter was placed within the building against which the pilot-scale landfill columns were secured. A hole was drilled through the building wall through which was placed a small bore plastic pipe. One end of the pipe was connected to the gas outlet positioned at the top of the columns, the other end being connected to the gas meter. The biogas from each column was measured every 5 days. The biogas vent from the columns being left open to atmosphere for the remaining 4 days. Leakage of biogas was noticed on Day 65.

The initial design of the columns featured a removable top cover, this was found to leak. Difficulties in effecting repairs were experienced. It was then decided to treat the top covers in an identical manner to the base of the column and to heat weld the HDPE plates to the column shell. This was successful. The consequences of these problems was monitoring of the evolution of the biogas was severely curtailed. It should be noted the experimental study involved 5 columns and it was not known when biogas evolution would start, and the volume of biogas that would be evolved; this further complicated matters.

The problems are shown chronologically below:

Day 65	Gas leakage first detected
Day 65 - Day 86	Repairs effected
Day 105	Repairs effected
Day 105 - Day 117	Only small amounts of biogas evolved, further leakage suspected
Day 117	HDPE heat welded onto the horizontal column shell
Day 118	Biogas monitoring resumed

Monitoring recommenced, but further problems were now experienced. Ambient temperatures began to fall with the onset of the southern hemisphere winter. Biogas production ceased completely from all of the pilot-scale columns on Day 128. The temperature of the columns had declined to below 10°C

When ambient temperatures began to rise at start of Spring, volumetric monitoring recommenced on Day 205. Monitoring continued until Day 348, biogas was not detected from any of the pilot-scale columns during this period. It was then decided to cease monitoring. It would appear the columns were now completely stabilised as no further evidence of biogas evolution was present. While biogas was present, the maximum biogas volumetric flowrates were:

Pilot-scale landfill column No. 1	7.01 ℓday^{-1}
Pilot-scale landfill column No. 2	4.78 ℓday^{-1}
Pilot-scale landfill column No. 3	7.01 ℓday^{-1}
Pilot-scale landfill column No. 4	0.57 ℓday^{-1}
Pilot-scale landfill column No. 5	1.16 ℓday^{-1}

(c) Analysis of biogas composition

Samples were taken from the biogas outlets on three occasions. A small plastic inflatable container was employed for this purpose. The flexible vessel was secured to the gas outlet, the biogas allowed to fill the container by means of its own pressure. The container was then evacuated, prior to securing to the biogas outlet, then allowed to fill twice, on the third expansion, this sample was retained for analysis. The composition of the gas was then determined by means of a Varian 3300 Gas Chromatograph.

Samples were taken on Day 93, Day 124 and Day 127. The results are shown below. It should be noted, numerous attempts were made to sample biogas but as the biogas production from the columns was limited, only the results below can be shown.

Table 4.10 Pilot-scale landfill columns: composition of generated biogas

Day	Sample	Percent methane	Percent carbon dioxide	Percent oxygen	Percent nitrogen
Day 93	Column 1	53.4	40.5	0.3	5.8
Day 124	Column 1	40.4	20.4	6.5	32.7
Day 127	Column 1	43.2	27.8	3.5	25.5
Day 93	Column 2	No	gas	production	
Day 124	Column 2	22.8	18.6	5.7	52.9
Day 127	Column 2	26.7	24.9	2.6	45.8
Day 93	Column 3	32.8	29.1	2.2	35.9
Day 124	Column 3	No	gas	production	
Day 127	Column 3	No	gas	production	
Day 93	Column 4	46.1	34.4	2.2	17.3
Day 124	Column 4	23.7	18.7	2.4	55.2
Day 127	Column 4	31.4	25.3	2.0	41.3
Day 93	Column 5	40.8	35.1	2.0	22.1
Day 124	Column 5	No	gas	production	
Day 127	Column 5	No	gas	production	

4.7.3 Residence Time Distribution - Pilot-scale landfill columns

A continuous reactor may behave in a manner comparable to a plug flow reactor or as a perfect mixer, but it can never achieve these idealised states. In an ideal plug flow reactor, all reactant and product molecules move at the same rate in the direction of the bulk fluid flow, while in real flow reactors, fluid velocity profiles, turbulent mixing, and molecular diffusion cause molecules to move with a variety of speeds and directions. These inevitable deviations in ideal reactor conditions lead to several fundamental problems in reactor design and analysis (Dudukovic *et al*, 1983).

Tracer response analysis is a technique which is used to characterise the type of flow and mixing that takes place in a continuous process vessel. The technique is also applicable to biological systems, hydrological systems, and in general, to any system through which a fluid flows continuously. In this case it is applied to the pilot-scale landfill columns.

The simplest method of determining the residence time distribution of a fluid within a reactor involves the use of a physical or non-reactive tracer. A number of different experimental techniques are available, the simplest to interpret are the pulse or the step experiment. For the purposes of this investigation it was decided to employ a non-reactive tracer with pulse input.

(a) Determination of non-reactive tracer

It is of importance that the tracer utilised should behave in a manner identically to the fluid molecules within the reactor. No tracer should be lost within the system by reaction or adsorption with the reactor walls, or internal packing, if present. The internal packing within the pilot-scale landfill columns is municipal solid waste; it was relevant to investigate the adsorption characteristics of any tracer selected with that substance. A frequently used non-reactive tracer employed in aqueous systems are the various salts of lithium. Lithium chloride is commonly used as a non-reactive tracer. Lithium is readily detectable in aqueous solutions with an atomic adsorption spectrometer, operating in the emission mode. The minimum lithium concentration detectable is approximately 0.2 $\mu g\ell^{-1}$ with a sensitivity of 0.04$mg\ell^{-1}$, the optimum working range being 0.1 to 2$mg\ell^{-1}$ (Standard Methods, 1992).

As the chloride content of landfill leachate is often at elevated levels, it was consequently decided to investigate the adsorption characteristics of lithium sulphate. Potable water would be added to the columns to replace the leachate drained from the column. Potable water in the Cape Town municipal area has a chloride content of approximately 27$mg\ell^{-1}$. The decrease in chloride content in the leachate, as the tracer response experiment progressed, could well serve as an inverse tracer if problems were experienced with the lithium sulphate tracer.

The TCLP was modified to enable the determination of the degree of adsorption of lithium sulphate onto municipal solid waste. The extraction fluid, with its acetate buffered system would appear to provide a good approximation of leachate from the pilot-scale landfill columns. The modification was effected in the following manner.

The solution was formulated, in the same manner as described previously (section 4.5.1). The pH of this solution was then adjusted with 1N sodium hydroxide until the pH of the solution was 6.8. This pH was decided upon as it was the average of all pH measurements taken of the leachate from the pilot-scale landfill columns at that time. Sufficient lithium sulphate was added to this solution for the lithium content to approximate 10$mg\ell^{-1}$. To assure the results of the lithium sulphate adsorption studies to be reproducible, and to eliminate any bias from the municipal solid waste it was decided to perform the experiments in triplicate. Again, one sample of the cumulative sample (sample 21) was used, the other two samples being differing sub-samples.

A 50g portion of the prepared municipal solid waste was weighed and placed in the extractor vessel. A 25mℓ sample of the lithium sulphate solution was then taken from the measuring cylinder. Exactly 1ℓ of the relevant pH-adjusted, dilute lithium sulphate solution was then added to the extractor vessel. The extractor vessel was then placed in the agitation device and agitation began. Agitation continued for a period of 32 hours.

After 32 hours had elapsed the agitator was stopped, another sample of volume 25mℓ was then taken for analysis. Details of the analysis, and degree of adsorption is shown below

Table 4.11 Adsorption of lithium at laboratory scale

Sample No.	Initial lithium concentration ($mg\ell^{-1}$)	Final lithium concentration ($mg\ell^{-1}$)	Percentage lithium adsorption
2	10.123	10.021	1.00
13	10.225	10.046	1.75
21	10.225	10.046	1.75

The percentage adsorption of lithium of less than 2 percent was considered acceptable and probably within experimental error for the analysis coupled with the degree of purity of the lithium sulphate employed.

(b) Mass of non-reactive tracer utilised

A solution of approximately 1 000mgℓ^{-1} of lithium, in the form of the sulphate salt was prepared. This solution was analysed in triplicate. The concentration of the solution was found to be 1 027mgℓ^{-1}. To determine the mass of lithium tracer to be added the following reasoning was applied. The total volume of water present in the pilot-scale columns approximated 400ℓ, the average weekly flowrates were approximately 35ℓ. There are two extreme *scenarios* to consider: if perfect plug flow conditions existed; if perfect mixing conditions were prevalent. If 1 000mg of lithium were added and the reactor functioned as a perfect mixer the outlet concentration would approximate 0.025mgℓ^{-1}. If the reactor functioned as a perfect plug flow reactor, the outlet concentration of lithium would approximate 29mgℓ^{-1}. Both these concentrations are detectable by the analytical procedure employed.

(c) Method of injection of non-reactive tracer

It was decided to use Column 4 for the residence time studies, this was an arbitrary decision. Leachate was withdrawn in the usual manner, the leachate being drained until the flow diminished to a slow drip. While the leachate was flowing a sample was taken for analysis. On these samples the following analyses were performed:

pH;
Electrical conductivity;
Chemical **O**xygen **D**emand (COD), unfiltered;
Chemical **O**xygen **D**emand (COD), filtered;
Chloride content;
Total Alkalinity;
Bicarbonate Alkalinity;
Orthophosphate and lithium content.

From the analyses of total alkalinity; bicarbonate alkalinity and orthophosphate, the volatile acid alkalinity was then calculated.

After the leachate flow diminished to a slow drip, the outlet valve from the pilot-scale column was then closed and the volume of leachate drained was measured. This was accomplished with a calibrated dip stick. The contents of the 80ℓ drainage tank were then pumped to waste. The same volume of potable water was then placed in the leachate drainage tank. At the top of the column exactly 1ℓ of the 1 000mgℓ^{-1} lithium solution was poured onto the aggregate distributor. The pump was then started, the contents of the drainage tank pumped to the top of the column, washing the tracer into the solid waste matrix.

(d) Monitoring of the non-reactive tracer

Every 7 days the leachate was drained; sampled; measured; and pumped to waste. The same volume of potable waste added to the drainage tank and pumped to the top of the pilot-scale landfill column. This exercise was repeated until chemical analysis revealed the lithium content of the sample of leachate diminished to a level similar to that of the first sample of leachate taken. The results were then examined to determine the residence time distribution of the landfill column, these are shown in Chapter 5 - Results and Calculations.

4.7.4 Pilot-scale evaluation of the kinetic and tracer studies

After the completion of the laboratory-scale experiments and the pilot-scale tracer response study, the results were examined. An initial requirement was that sufficient copper-chromium-arsenic solution was co-disposed with the municipal solid waste in the column to obtain a response in the liquid effluent from the column. The following data were revealed from the laboratory-scale experiments:

the quantity of the metals adsorbed by the municipal solid waste;
the rate of that adsorption

The pilot-scale tracer study revealed the residence time distribution within the column. Results indicated adequate time for the adsorption reactions to reach completion. To estimate the mass of copper-chromium-arsenic solution the maximum adsorption was initially calculated. This was calculated in the following manner.

Mass of municipal solid waste in laboratory scale experiments = 50g
Mass of municipal solid waste in pilot-scale column ≈ 668kg

Example

Average mass of copper sorbed at pH7.0 = 23mg
Maximum mass of copper adsorbed at pilot-scale = (23/50)×668 = 308g

The calculation was completed for all relevant pH values, the results are shown in Table 4.12, below.

Another factor that was considered before the addition of the solution was particle size. The municipal solid waste was reduced in size to below 1mm for the laboratory scale kinetic trials. The solid waste employed in the pilot-scale columns was reduced in size to between 25 and 40mm. The surface area presented for adsorption would consequently be vastly different.

Table 4.12 Maximum adsorption of the copper, chromium and arsenic

Metal	pH	Average Mass sorbed (mg)	Average Mass sorbed (mg g^{-1})	Anticipated adsorption (g)
Copper	5.5	50.9	1.02	681
	6.4	14.1	0.28	187
	7.0	23.0	0.46	307
Chromium	5.5	53	1.06	708
	6.4	31	0.62	414
	7.0	21	0.42	281
Arsenic	5.5	70	1.40	935
	6.4	36	0.72	481
	7.0	41	0.82	548

The copper-chromium-arsenic solution is supplied by the manufacturer in the following composition (section 4.4.1). Copper, is present at 93.1 $g\ell^{-1}$, chromium is present at 269.6$g\ell^{-1}$, and arsenic is present at 270.2$g\ell^{-1}$. It can be seen from Table 4.12, at pH7.0, the probable leachate pH, the expected masses of metal to be adsorbed were:

Copper = 307g
Chromium = 281g
Arsenic = 548g

It was anticipated that virtually all the copper would precipitate within the column, thus attention was focused upon the chromium and the arsenic. If the approximate minimum mass of arsenic was added (548g), then approximately the same mass of chromium would be added, from the calculations above this would greatly exceed the expected adsorption, and additionally no allowance had been made for particle size. It was then considered sufficient to add near the theoretical maximum of chromium (281g), the difference in particle size and hence surface area should allow both chromium and arsenic to be present in the leachate.

The volume of copper-chromium-arsenic added to the municipal solid waste was 950mℓ, the mass of metals added is shown below:

Mass of chromium added	=	256.1g
Mass of copper associated	=	88.4g
Mass of arsenic associated	=	256.8g

(a) Experimental procedure - co-disposal of copper-chromium-arsenic solution

It was decided to use Columns 3 and 5 for the co-disposal studies as these columns had exhibited the most consistent volumetric leachate flowrates. Leachate was withdrawn in the usual manner, the leachate being drained until the flow diminished to a slow drip. While the leachate was flowing, a sample was taken for analysis. On these samples the following analyses were performed:

pH;
Electrical conductivity;
Chemical **O**xygen **D**emand (COD), unfiltered;
Chloride content;
Copper content;
Chromium content;
Arsenic content.

After the leachate flow diminished to a slow drip, the outlet valve from the pilot-scale column was then closed and the volume of leachate drained was measured. This was accomplished with a calibrated dip stick. The contents of the 80ℓ drainage tank were then pumped to waste. The same volume of potable water was then placed in the leachate drainage tank. At the top of the column exactly 950mℓ of the concentrated copper-chromium-arsenic solution was poured onto the aggregate distributor. The pump was then started, the contents of the drainage tank pumped to the top of the column washing the solution into the solid waste matrix.

(b) Monitoring of the pilot-scale co-disposal experiment

Every 7 days the leachate was drained; sampled; measured; and pumped to waste. The same volume of potable waste added to the drainage tank and pumped to the top of the pilot-scale landfill column. This exercise commenced on Day 567 and was repeated until Day 754. The results were then examined to determine the degree of agreement between the laboratory and pilot-scale studies. The results are shown in Chapter 5 - Results and Calculations.

4.8 ANALYTICAL PROCEDURES

Chemical analysis was performed at the laboratory of the Department of Chemical Engineering of the University of Cape Town, and at the laboratory of the Scientific Services Branch, City Engineer's Department, City of Cape Town. In some instances analysis was duplicated, being accomplished at both establishments to ensure accuracy.

Analysis of the kinetics experiments was such an instance. The initial analysis of copper chromium, and arsenic was undertaken at the Department of Chemical Engineering. Copper and chromium analysis was then repeated at Scientific Services Branch on approximately 25 percent of the samples to ensure accuracy. In the case of copper agreement was excellent; some degree of instrument drift was noted in the analysis of chromium; the relevant samples were re-analysed when necessary.

Table 4.13 Analytical responsibilities

Component	Establishment
Characterisation of the municipal solid waste	Scientific Services Branch
Characterisation of the copper-chromium-arsenic wood preservative	Department of Chemical Engineering
Laboratory scale equilibrium and kinetic trials	Department of Chemical Engineering, certain samples being repeated at the Scientific Services Branch
Leachate analysis	Scientific Services Branch
Biogas analysis	Scientific Services Branch

4.8.1 Characterisation of the municipal solid waste

The municipal solid waste was analysed for the following:
Moisture content; copper; chromium; zinc; cadmium; nickel; lead; potassium; phosphorous; pH; percentage volatile solids; and total kejldahl nitrogen.

4.8.2 Characterisation of the copper-chromium-arsenic wood preservative

The wood preservative was analysed for copper; chromium and arsenic.

4.8.3 Laboratory scale investigation: equilibrium and kinetics studies

All samples taken were analysed for copper, chromium and arsenic

4.8.4 Biogas

Biogas was analysed for percentage: methane; carbon dioxide; oxygen and nitrogen.

4.8.5 Leachate - tracer response study

Leachate was analysed for: pH; electrical conductivity; **C**hemical **O**xygen **D**emand (COD), unfiltered; **C**hemical **O**xygen **D**emand (COD), filtered; chloride content; total alkalinity; bicarbonate alkalinity; orthophosphate and lithium content.

4.8.6 Leachate - pilot-scale co-disposal studies

Leachate was analysed for: pH; electrical conductivity; **C**hemical **O**xygen **D**emand (COD), unfiltered; chloride content; copper content; chromium content; arsenic content.

4.8.7 Analytical equipment

At Scientific Services Branch the following equipment was employed:

Table 4.14 Analytical equipment

Analysis	**Instrument**
Conductivity	EDT Instruments BA 380
pH	Orion Research Model 601
Gas analysis	Varian 3300 Gas Chromatograph
Metal content	GBC Model 902 Atomic Adsorption Spectrophotometer

The analysis of metals was undertaken at the University of Cape Town, a Varian SpectrAA 30 Atomic Adsorption Spectrophotometer was employed.

4.9 SUMMARY

The chemical engineering principles of reactor design were employed to determine the behaviour of heavy metals within the landfill environment. The metals examined were copper, chromium and arsenic, in the form of CCA (or Tanalith). The kinetics of adsorption/desorption of this substance were appraised at laboratory scale. Pilot-scale landfill columns were constructed at Athlone, Cape Town. Tracer studies were then undertaken at pilot-scale. The combination of the results from the kinetic studies and the results from the tracer studies allow the computation of the exit stream composition. Heavy metals were then co-disposed at pilot-scale to evaluate the accuracy or otherwise of both the tracer studies and the chemical kinetics. The results will now be applied to the full scale landfill. The municipal solid waste placed in the columns; the liquid effluent (leachate) the gaseous effluent (biogas) were fully analysed in terms of mass (or volume) and composition. This allowed characterisation of the reactor system as a whole, and

permits the experimental results to be evaluated knowing the degree of degradation of the municipal solid waste.

CHAPTER 5
RESULTS AND CALCULATIONS

5.1 INTRODUCTION

As reported in Chapter 4, the experimental programme comprised of two complimentary investigations:

(i) Laboratory scale investigation;
(ii) Pilot-scale investigation.

These two complimentary investigations were then further sub-divided into manageable, associated elements.

Laboratory scale investigation
The laboratory scale investigation was also constituted of two integral sections:
Evaluation of kinetic rate constants, adsorption and desorption;
evaluation of adsorption isotherms.

Pilot-scale investigation
This investigation advanced on two fronts:
Evaluation of the residence time distribution/deviation from ideal behaviour of the pilot-scale landfill columns.
Evaluation, at pilot-scale, of the kinetic rate constants determined at laboratory scale.

5.2 LABORATORY SCALE INVESTIGATION

5.2.1 Results from the Adsorption studies

Adsorption studies were undertaken at three pH values; pH5.5, pH6.4, and pH7.0. Initial (0.0h) and final (32.0h) results from the kinetic studies were also utilised in the construction of the adsorption isotherms. The results are shown in Appendix B, Table B-1 (pH5.5); Table B-2 (pH6.4); Table B-3 (pH7.0). Freundlich isotherms were successfully constructed for copper at pH values 5.5 and 7.0; for chromium and arsenic at all three pH values, 5.5, 6.4 and 7.0. The constructions are shown in section 5.4.2

5.2.2 Results from the kinetics studies

The kinetics experiments were undertaken in triplicate, at three pH values, 5.5 (coded A, B and C) 6.4 (coded D, E and F) and 7.0 (coded G, H and I). As reported in section 4.5, the experimental method made available data for analysis of the kinetics of adsorption and desorption of the metallic ions. The adsorption results are reported as analysed in the laboratory and are shown in Appendix B, Table B-4 (pH5.5); B-5 (pH6.4) and B-6 (pH7.0).

The desorption results are reported Table B-7 (pH5.5); B-8 (pH6.4) and B-9 (pH7.0). Graphical representations of the analytical results from the adsorption kinetic trials are shown overleaf (Figures 5.1 to 5.27). As with most experimental data, a degree of scatter can be observed in the experimental results, this is addressed in the interpretation of the data in section 5.4.3. The degree of scatter is however, most noticeable at the lower experimental time frames. Chemisorption is often preceded by physical adsorption, which is easily reversible (section 2.8.1.3(b)). This would explain the scattering of data points at short experimental times. The ions being only loosely bound by physical adsorption to the solid waste matrix, at low experimental values of time.

In all cases, sorption of the metallic ions is characterised by a rapid initial sorption, the sorption rate decreasing with increased time. The analogy between the adsorption of solutes onto soils has been discussed (section(s) 2.8.1.3(a) and 3.3). Rapid soil reactions are, in general, reactions which transport at the solid phase do not significantly influence the reaction rate. Conversely, slow reactions are often characterised by diffusional mass transfer limitations (section 3.3.2). On initial inspection, these conditions would appear apparent. This phenomena, together with a proposed reaction mechanism is discussed fully in Chapter 6.

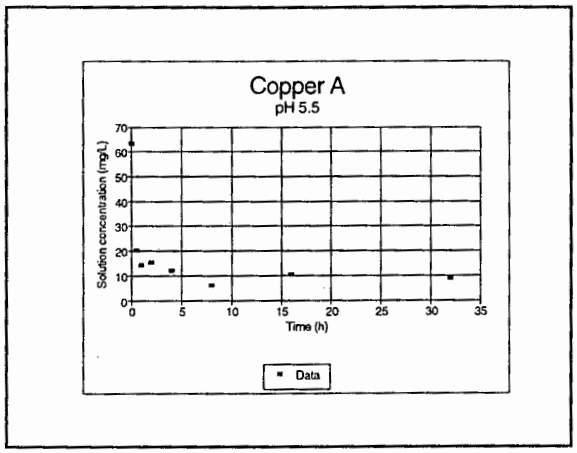

Figure 5.1
Adsorption of copper (A): pH 5.5

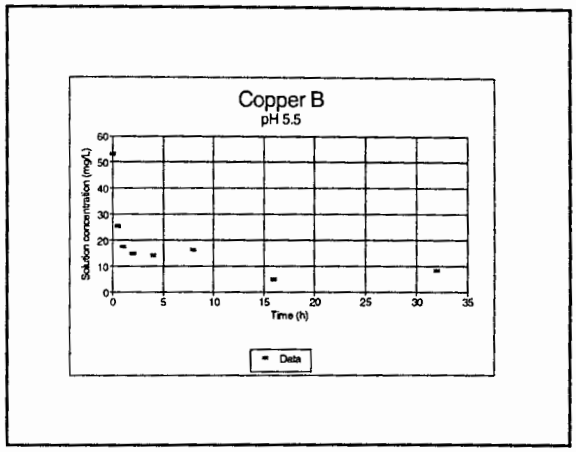

Figure 5.2
Adsorption of copper (B): pH 5.5

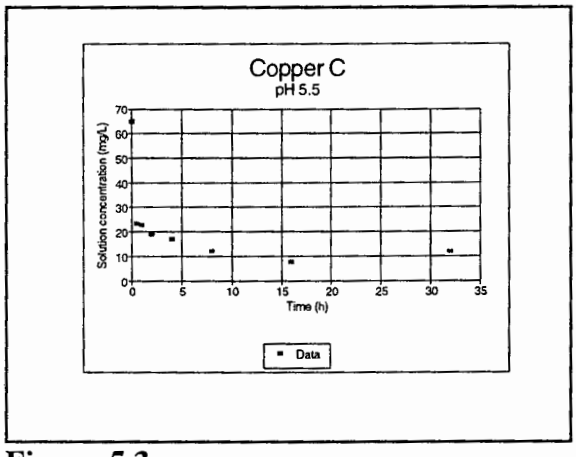

Figure 5.3
Adsorption of copper (C): pH 5.5

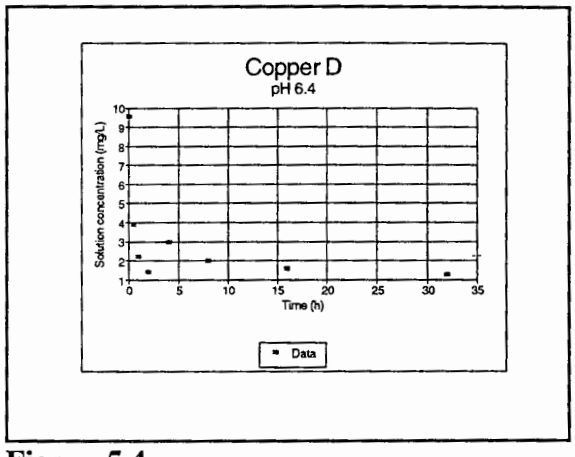

Figure 5.4
Adsorption of copper (D): pH 6.4

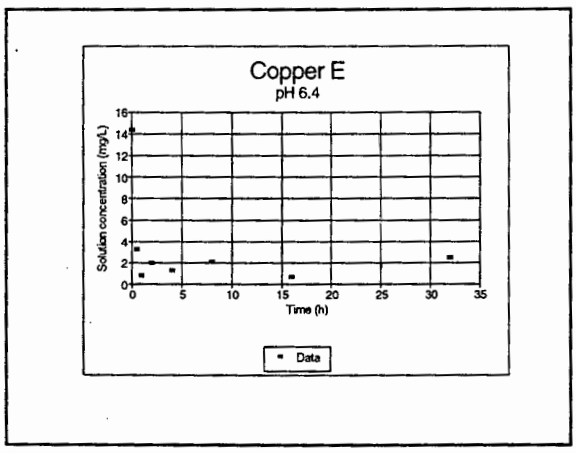

Figure 5.5
Adsorption of copper (E): pH 6.4

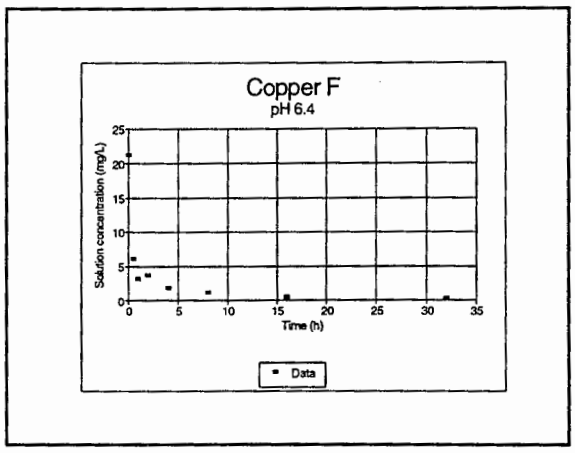

Figure 5.6
Adsorption of copper (F): pH 6.4

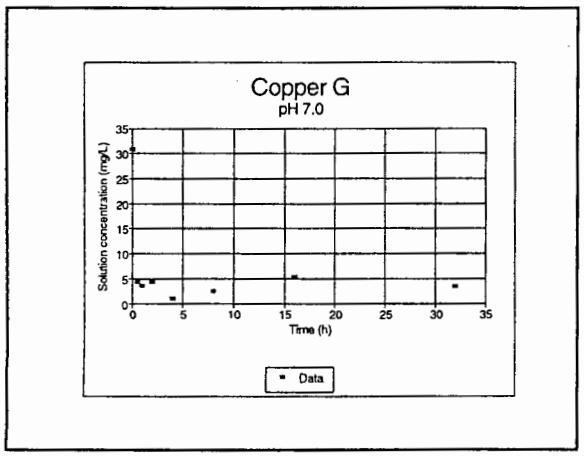

Figure 5.7
Adsorption of copper (G): pH 7.0

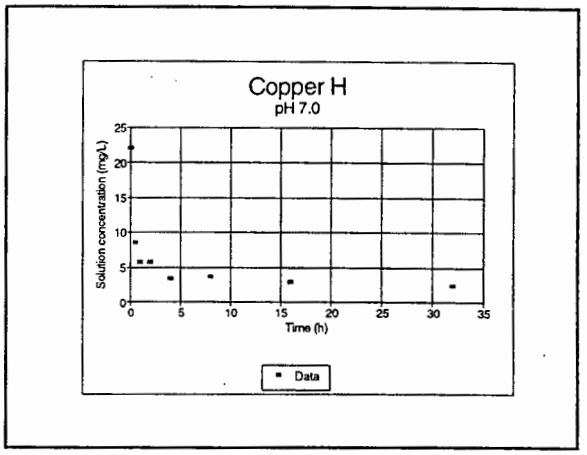

Figure 5.8
Adsorption of copper (H): pH 7.0

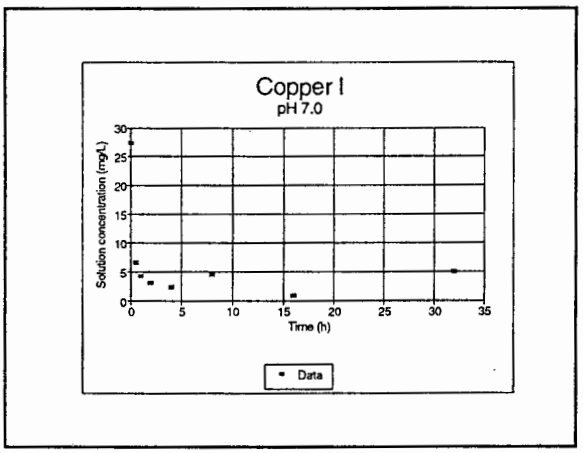

Figure 5.9
Adsorption of copper (I): pH 7.0

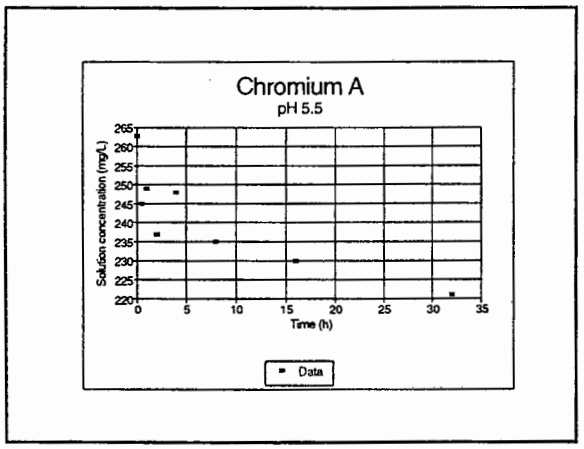

Figure 5.10
Adsorption of chromium (A): pH 5.5

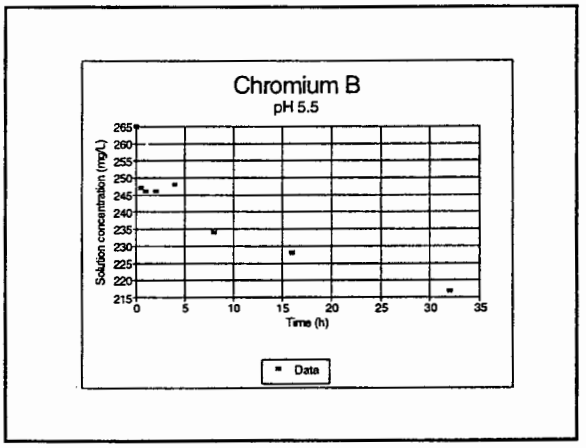

Figure 5.11
Adsorption of chromium (B): pH 5.5

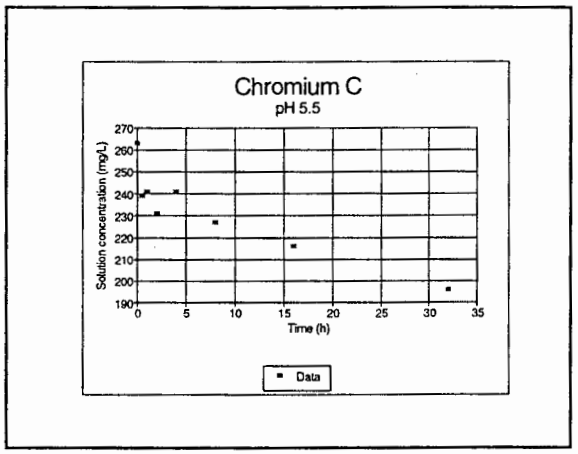

Figure 5.12
Adsorption of chromium (C): pH 5.5

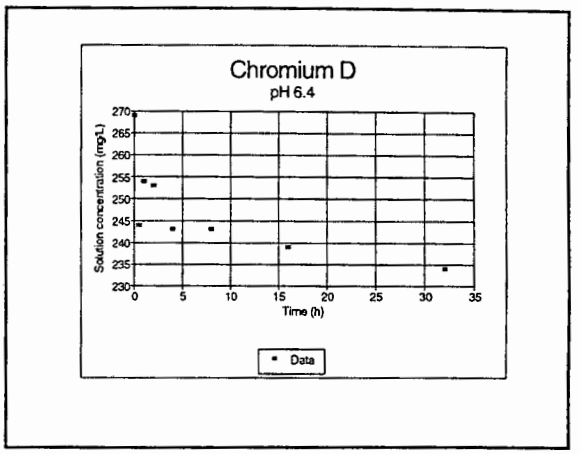

Figure 5.13
Adsorption of chromium (D): pH 6.4

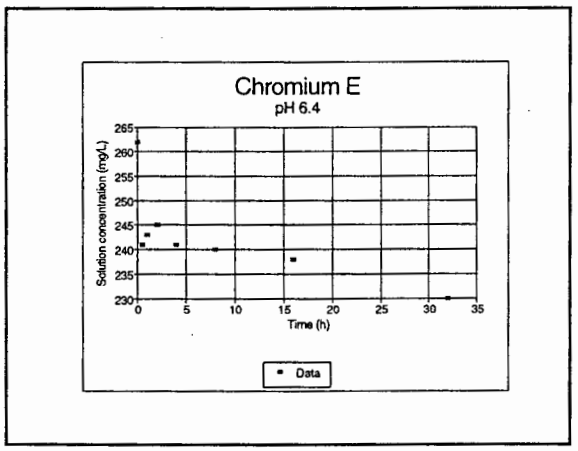

Figure 5.14
Adsorption of chromium (E): pH 6.4

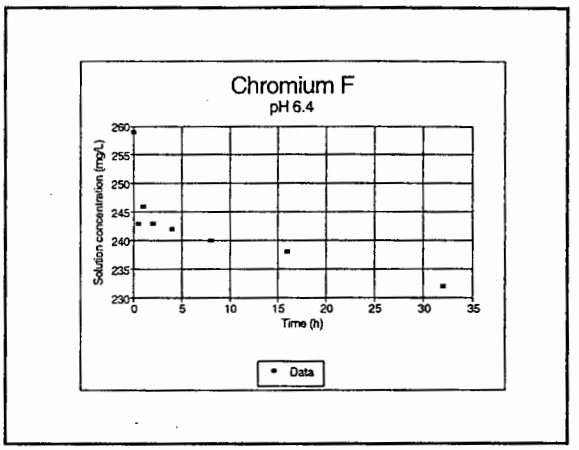

Figure 5.15
Adsorption of chromium (F): pH 6.4

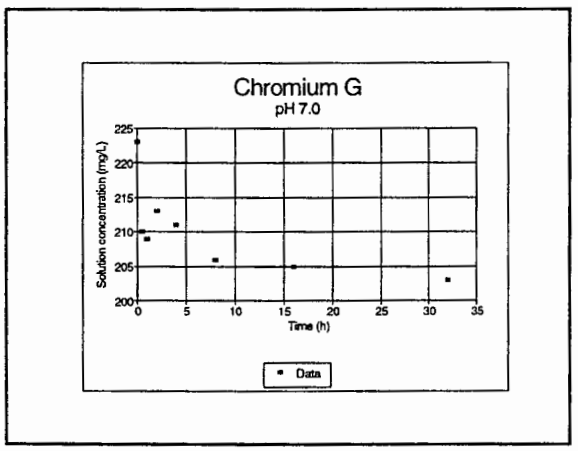

Figure 5.16
Adsorption of chromium (G): pH 7.0

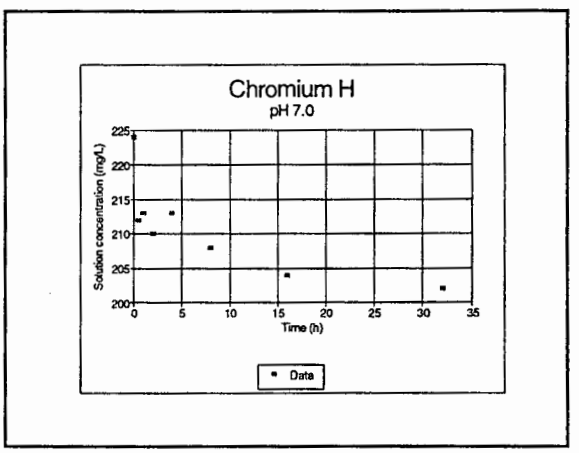

Figure 5.17
Adsorption of chromium (H): pH 7.0

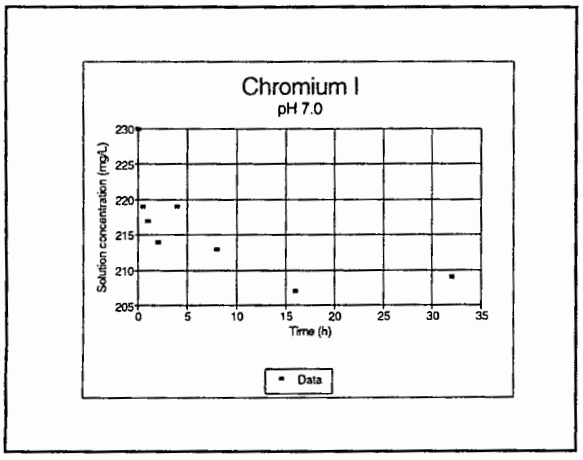

Figure 5.18
Adsorption of chromium (I): pH 7.0

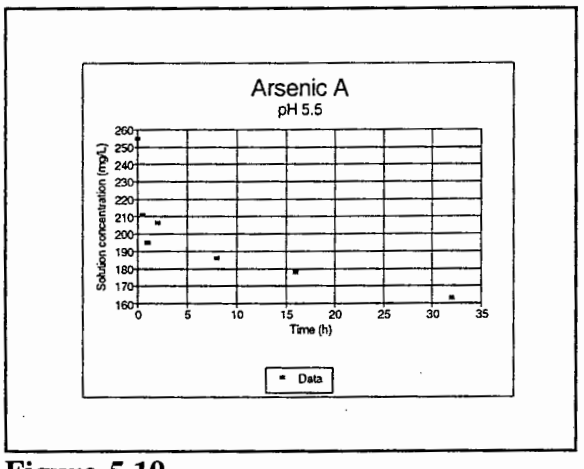

Figure 5.19
Adsorption of arsenic (A): pH 5.5

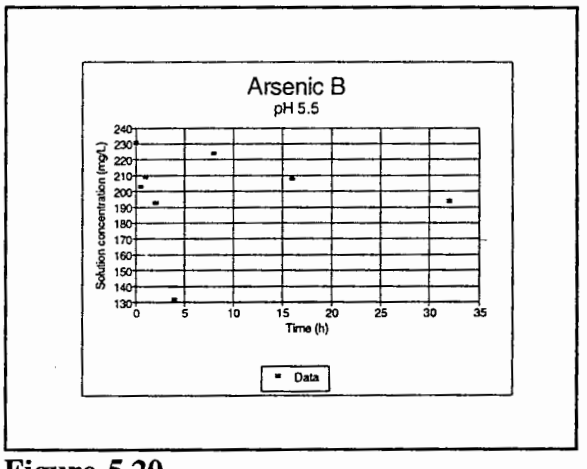

Figure 5.20
Adsorption of arsenic (B): pH 5.5

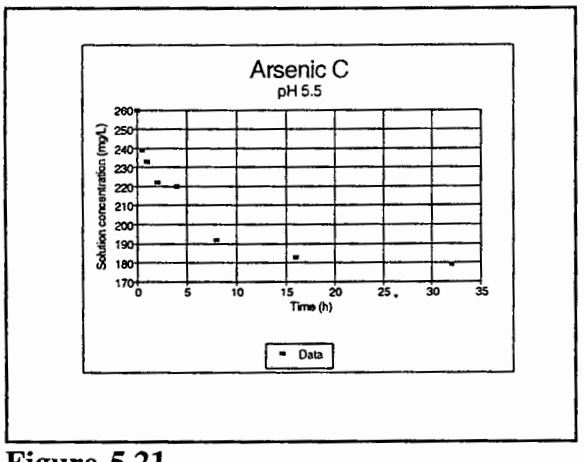

Figure 5.21
Adsorption of arsenic (C): pH 5.5

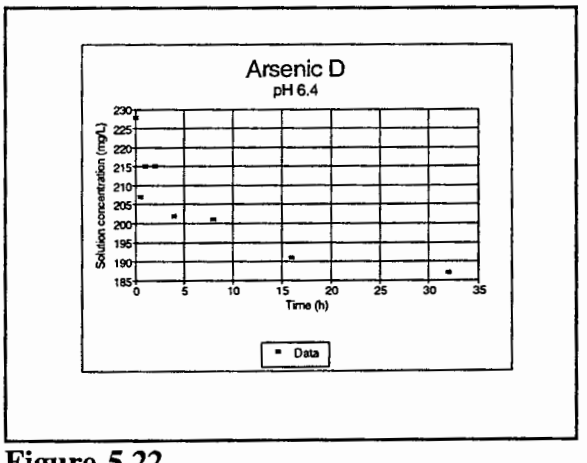

Figure 5.22
Adsorption of arsenic (D) : pH 6.4

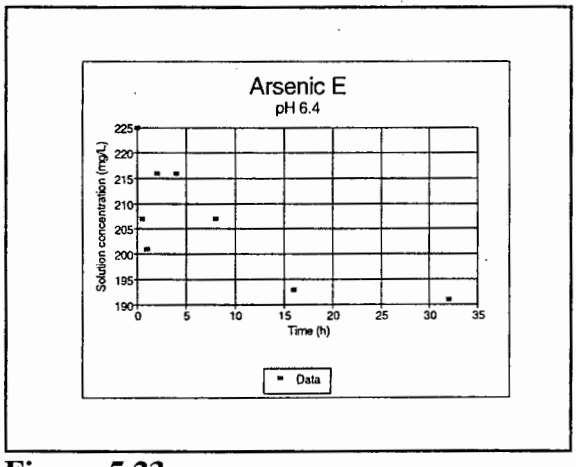

Figure 5.23
Adsorption of arsenic (E): pH 6.4

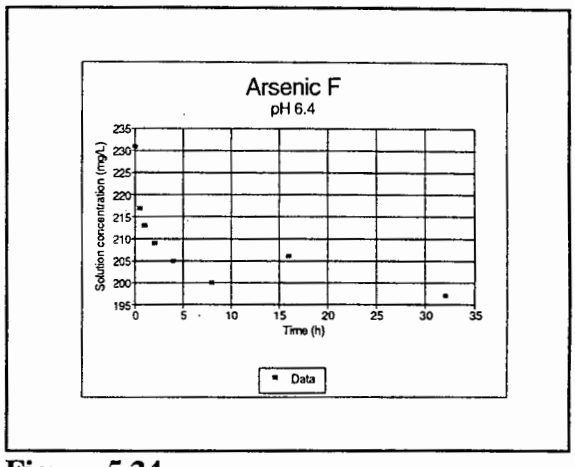

Figure 5.24
Adsorption of arsenic (F): pH 6.4

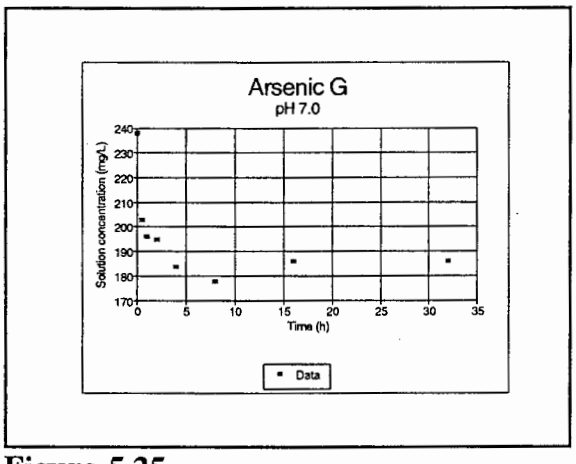

Figure 5.25
Adsorption of arsenic (G): pH 7.0

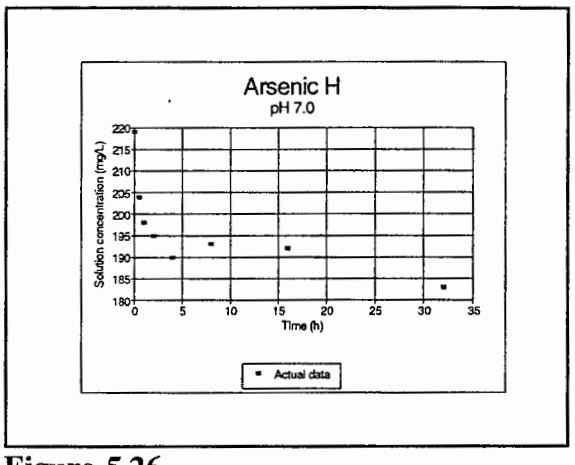

Figure 5.26
Adsorption of arsenic (H): pH 7.0

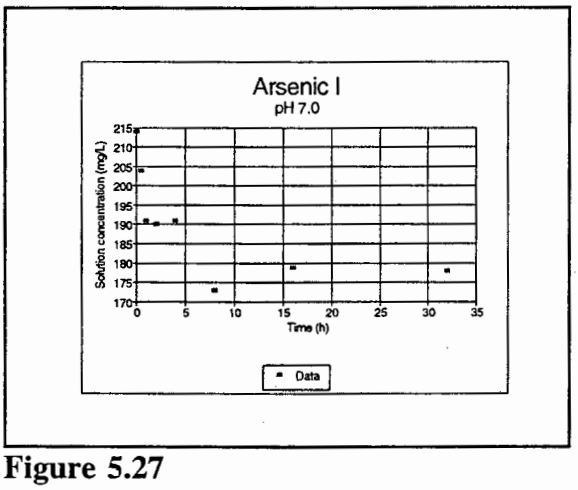

Figure 5.27
Adsorption of arsenic (I): pH 7.0

5.3 PILOT-SCALE INVESTIGATION

5.3.1 Leachate recirculation

As reported in Chapter 4, leachate first became evident on Day 60. Leachate was drained until the flow diminished to a slow drip. The volume of leachate obtained was measured on cessation of flow. While the leachate was flowing a sample was taken for analysis. On these samples the following analyses were performed:

pH;
Electrical conductivity;
Chemical Oxygen Demand (COD), unfiltered;
Chemical Oxygen Demand (COD), filtered;
Chloride content;
Total Alkalinity;
Bicarbonate Alkalinity;
Orthophosphate.

From the analyses of total alkalinity; bicarbonate alkalinity and orthophosphate, the volatile acid alkalinity was then calculated. Results of the chemical analysis, together with the volume of leachate drained, are shown in Appendix C.

The recirculation procedure was performed every 7 days, until Day 118. Recirculation ceased at this point as the temperature inside the columns had dropped to below 15°C, and there was no evidence of biogas production. The lower temperatures were due to the onset of the South African winter season.

Recirculation of leachate recommenced on Day 231; ambient temperatures were beginning to rise, as the southern hemisphere summer season was beginning. The recirculation procedure then continued as before; the procedure being repeated after a time interval of 7 days. The procedure was discontinued on Day 358, as there was no resumption of biogas production. Column 4 was only recirculated until Day 118. From Day 231, column 4 was employed for tracer studies. The results obtained until Day 118 for column 4 are shown in Appendix C, Table C-5. The results obtained from columns 1, 2, 3 and 5 are discussed briefly below.

The average pH of leachate from columns 1, 2, 3 and 5 averaged 7.0. The highest pH value recorded was 7.3, the lowest was 6.6. Initial measurements of electrical conductivity were performed on an undiluted sample. It was found the measurements varied and were inconsistent. This method of analysis continued until Day 110, thereafter leachate was diluted, and the value of electrical conductivity reported was adjusted to the degree of dilution. Electrical conductivity measurements (from Day 110) were relatively consistent from all the columns (apart from the occasional high or low value), and averaged 1 068mSm^{-1} from column 1; 1 050mSm^{-1} from column 2; 1 042mSm^{-1} from column 3, and 1 029mSm^{-1} from column 5.

Leachate was analysed for COD in the un-filtered and filtered, state. This was a

precautionary measure, as it was initially considered the presence of particulate matter would adversely affect data trend analysis. The COD content of the leachate showed an initial rapid reduction from approximately 6 000mgℓ^{-1} to approximately 2 000mgℓ^{-1} during the first 110 days. The COD continued to decrease until leachate recirculation ceased on Day 358. The COD then approximated 1 200mgℓ^{-1} in the unfiltered samples. All of the columns exhibited similar behaviour.

Chloride levels remained consistent throughout the recirculation period; there was little difference in chloride measurements from individual columns. Chloride content averaged 1077mgℓ^{-1} from column 1; 1 154mgℓ^{-1} from column 2; 1 052mgℓ^{-1} from column 3; 998mgℓ^{-1} from column 5. Both total alkalinity and bicarbonate alkalinity gradually decreased throughout the duration of the recirculation, the total alkalinity decreasing from approximately 4 500mgℓ^{-1} to 3 800mgℓ^{-1}. The bicarbonate alkalinity showed a similar trend the values being consistently lower by approximately 300mgℓ^{-1}. The volatile acid alkalinity of leachate from the columns showed an initial sharp decrease from approximately 550mgℓ^{-1} to 300mgℓ^{-1}, and stabilised at this value for the duration of the experiment. Levels of ortho-phosphate in the leachate showed a similar trend from all the columns. The results were extremely erratic over the duration of leachate recirculation, but decreased to very low levels (0.1mgℓ^{-1}) by Day 358.

Results from previous column studies conducted at the University of Cape Town employing "fresh" municipal solid waste are extremely well documented (Chapman *et al* 1991). After 50 weeks of recirculating leachate the researchers reported the following results: pH levels of 5.7; COD levels of 27 000mgℓ^{-1} ; bicarbonate alkalinity of 120mgℓ^{-1} ; volatile acid alkalinity of 13 000mgℓ^{-1} ; electrical conductivities approximating 1 500mSm^{-1}; ortho-phosphate, 15mgℓ^{-1} . The columns did not generate biogas, acetogenic conditions were evident. The United Kingdom's Department of Environment (DOE, 1986) report values of leachate from "aged wastes". Reported are, pH values of 7.5; COD levels of 1 160mgℓ^{-1} and phosphate levels of approximately 1mgℓ^{-1}. This, together with the low levels of biogas production from the columns (section 4.7.2(b)), confirm the municipal solid waste was well stabilised prior to placement within the pilot-scale landfill columns.

5.3.2 Lithium sulphate pulse experiment

Results from the lithium sulphate pulse experiment are shown in Appendix D. Table D-1 details the volumetric displacement of leachate; the lithium concentration of the leachate; the mass of lithium obtained per sample, and the cumulative mass of lithium. Table D-2 characterises the leachate in terms of pH, COD, etc.. The mass of lithium sulphate introduced in the system was 1 027.7mg, of this 954.3mg was successfully recovered, a recovery rate of 92.9 percent. The time duration of the experiment was 317 days, the average volumetric displacement of leachate was 36.5ℓweek^{-1} . Maximum lithium recovery occurred after 84 days, the lithium concentration of the leachate at that time was 2.003mgℓ^{-1}. Leachate was sampled and recirculated approximately every 7 days. The volumetric displacement of leachate from the column varied, and additionally, on occasion, sampling and recirculation could not be effected on the designated day. The conventional graphical representation used reporting results of this nature is in terms of concentration-time, because of the variation in both volumetric displacement and on occasion, time increments, a far more satisfactory

representation of the experimental data is mass (of lithium in leachate) versus time. This shown below in Figure 5.28

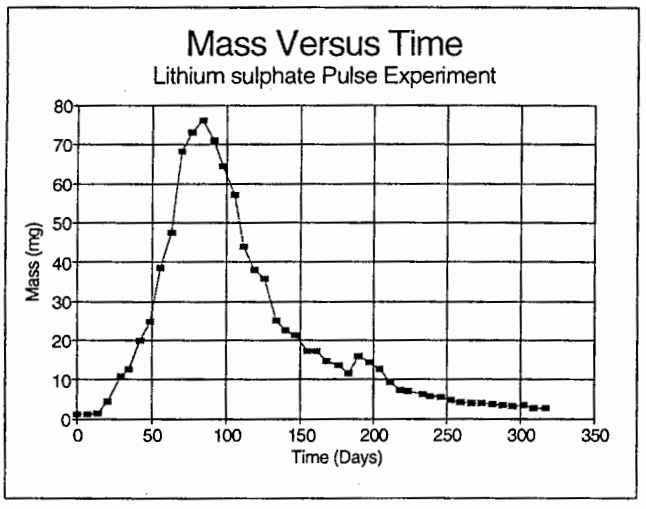

Figure 5.28
Results of lithium pulse experiment

The mass-time curve reveals a system that is non-ideal. In an industrial reactor of this nature i.e. a packed column, assuming ideal behaviour, one would anticipate plug flow. The graphical representation of the data should then resemble a thin spike located at maximum tracer concentration. The large base is indicative of axial dispersion of the fluid; the early initial commencement of the curve is a manifestation of channelling; the long tail is symptomatic of stagnant areas within the column. The curve is however, consistent, except for a small secondary peak occurring around Day 200. This phenomena is indicative of stagnant flow areas within the column. The only deviation from ideality that one would not experience on a full scale landfill is the high degree of initial channelling. It is probable that wall effects from the column are a contributory factor. The curve is further examined in section 5.4.5.

*(a) **Chemical characteristics of leachate collected during the lithium pulse experiment***
As would be expected when draining leachate to waste, and replacing the leachate with an equal volume of fresh potable water, all the determined chemical parameters (except for pH) showed a steady decline. Initial COD levels approximated 2 000mgℓ^{-1} reducing to just above 100mgℓ^{-1}, chloride levels diminished from 900mgℓ^{-1} to around 40mgℓ^{-1} while electrical conductivity decreased from 1 100mSm^{-1} to about 200mSm^{-1}.

5.3.3 Co-disposal of copper, chromium and arsenic at pilot-scale

As reported in section 4.7.4, a concentrated solution of copper, chromium and arsenic was co-disposed with the municipal solid wastes in columns 3 and 5. Analytical results are reported in Appendix E. Tables E-1 and E-3 tabulate leachate volumes and metal concentrations for columns 3 and 5 respectively; Tables E-2 and E-4 tabulate the associated chemical data (pH, COD, etc.,) for columns 3 and 5. The mass of metals introduced into both columns 3 and 5 was copper, 88.4g; chromium, 256.1g and arsenic, 256.7g. The time duration of the experiment with column 3 was 235 days, the average volumetric displacement

of leachate was 19.2ℓweek^{-1}. The time duration of the experiment with column 5 was slightly shorter, 221 days. The average displacement of leachate was 18.5ℓweek^{-1} . The volumetric displacement of leachate, although similar to column 3, tended to vary slightly more.

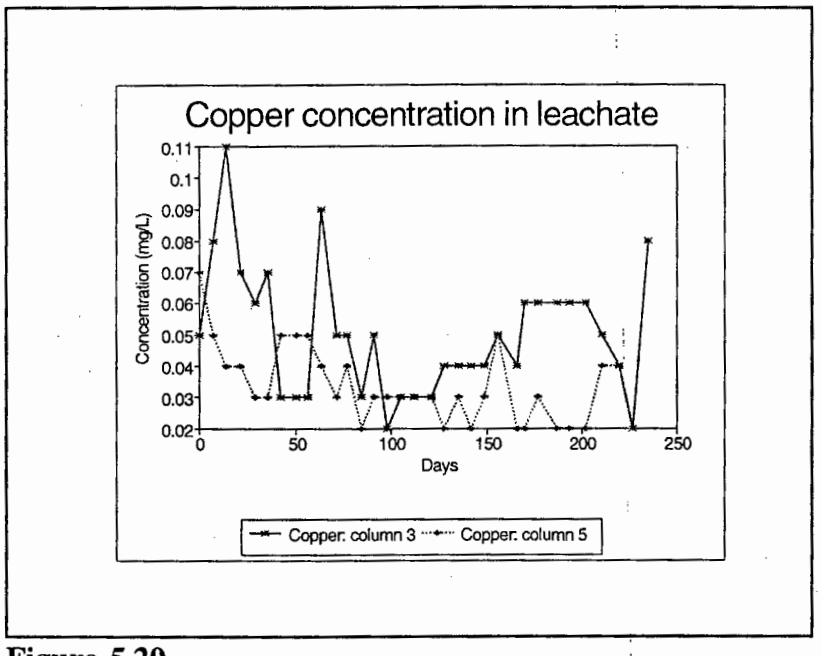

Figure 5.29
Copper concentration in leachate from columns 3 and 5

(a) Copper content in leachate from columns 3 and 5

Results from the monitoring of copper concentration of leachate from columns 3 and 5 are shown graphically in Figure 5.29. The initial concentration of copper in the leachate from column 3 was 0.05mgℓ^{-1}, after 14 days the copper concentration in the leachate had risen to 0.11mgℓ^{-1}, the highest concentration recorded. This initial rise in copper concentration was probably caused by rapid liquid flow through the column symptomatic of a combination of preferential fluid channelling and wall effects. Subsequently, the copper concentration was lower at 0.04mgℓ^{-1}, slightly lower than the initial base-line reading of 0.05mgℓ^{-1}. From Day 170 to Day 202, the copper concentration stabilised at 0.06mgℓ^{-1}. At Day 235 the copper concentration was slightly elevated at 0.08mgℓ^{-1}. Over the entire period of monitoring (235days), the concentration of copper in the leachate from column 3 averaged 0.05mgℓ^{-1}, i.e. no higher than the initial reading at Day zero.

The initial concentration of copper in the leachate from column 5 was 0.07mgℓ^{-1} a value that was not exceeded for the entire duration of the experiment. The final copper concentration after 221 days was 0.04mgℓ^{-1}. Over the entire period of monitoring (221days), the concentration of copper in the leachate from column 3 averaged 0.03mgℓ^{-1}.

(b) Chromium content in leachate from columns 3 and 5

Results from the monitoring of chromium concentration of leachate from columns 3 and 5 are shown graphically in Figure 5.30. Initially, chromium in the leachate from column 3 was not detectable. The chromium content of the leachate rose steadily over the next 90 days to 0.04 mgℓ^{-1}, this value was not exceeded for the duration of the experiment, the final chromium concentration was 0.03mgℓ^{-1} on Day 235. The average chromium content in the leachate from column 3 over the entire duration of monitoring was 0.03mgℓ^{-1}

The initial chromium content of leachate from column 5 was 0.06mgℓ^{-1}, this dropped, and then steadily rose to 0.06mgℓ^{-1} by Day 90. The chromium concentration then stabilised at

approximately this level until Day 180, whereafter metal content dropped very slightly. The final chromium concentration was 0.02 mgℓ^{-1} on Day 221. The average chromium content in the leachate from column 5 over the entire duration of monitoring was 0.04mgℓ^{-1}.

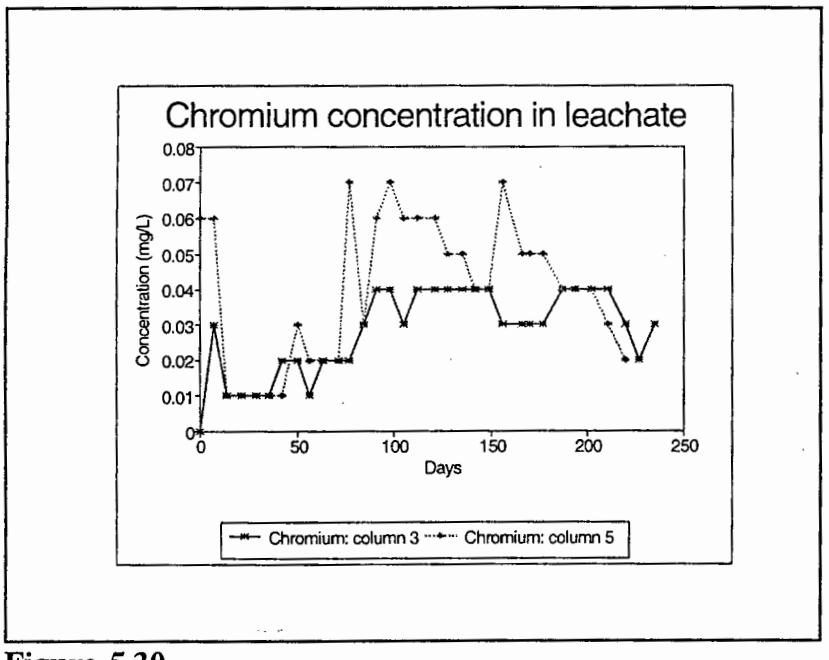

Figure 5.30
Chromium concentration in leachate from columns 3 and 5

(c) Arsenic content in leachate from columns 3 and 5

The behaviour of the co-disposed arsenic was by far the most interesting of the three metals. Results from the monitoring of arsenic concentration of leachate from columns 3 and 5 are shown graphically in Figure 5.31. The initial concentration of the arsenic in the leachate from column 3 was 17μgℓ^{-1} rising in a near exponential manner to Day 135 where the arsenic concentration exceeded 1000μgℓ^{-1}. Subsequently, the concentration of arsenic in the leachate reduced to approximately 830μgℓ^{-1} and stabilised at that level until Day 194 when the concentration exceeded 2000μgℓ^{-1}. Arsenic concentration in the leachate

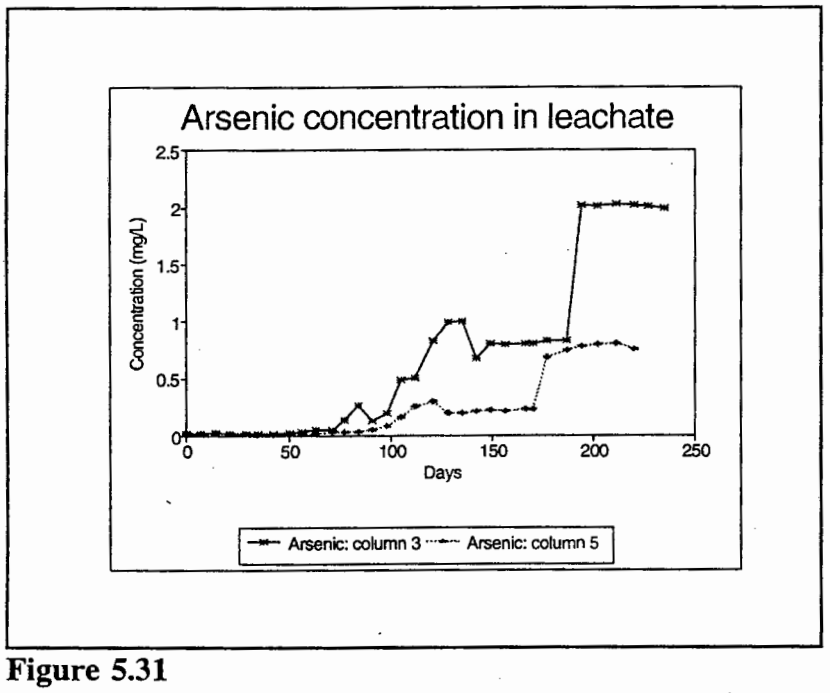

Figure 5.31
Arsenic concentration in leachate from columns 3 and 5

from column 3 remained at that level until the cessation of monitoring on Day 235. Column 5 mirrored the behaviour of column 3, though, at a reduced manner. The maximum arsenic concentration attained was 802$\mu g\ell^{-1}$ at Day 213; results were relatively constant from Day 188 at that level.

(d) Chemical characteristics of the leachate from columns 3 and 5

The chemical characteristics of the leachate from both columns 3 and 5 were very similar. Initial COD levels approximated 1 200 reducing to 400mgℓ^{-1}, chloride levels diminished from 1 000mgℓ^{-1} to around 200mgℓ^{-1} while electrical conductivity decreased from 500mSm^{-1} to about 300mSm^{-1}.

5.4 CALCULATIONS

5.4.1 Adsorption Isotherms

(a) Freundlich Isotherm

The Freundlich or van Bemmelen equation may be expressed as:

$$q = K_F C_e^M \qquad 3.1$$

Where,

q	=	solute adsorbed per unit weight of solid adsorbent
K_F	=	Freundlich equilibrium distribution coefficient
C_e	=	Concentration of solute remaining in fluid at equilibrium
M	=	Freundlich power coefficient

Data are usually fitted to the logarithmic form of the equation:

$$\ln(q) = M * \ln(C_e) + \ln(K_F)$$

If the Freundlich adsorption isotherm is suitable, a logarithmic plot of solute adsorbed (q) versus equilibrium solute fluid concentration (C_e) results in a straight line with a slope equal to the Freundlich power coefficient (M) and an intercept equal to the value of the logarithmic form of the Freundlich equilibrium distribution coefficient (K_F)

(b) Method of examination of adsorption data

Initially, a logarithmic plot of solute adsorbed(mg) versus solute equilibrium concentration (mgℓ^{-1}) was constructed. This plot was then examined for any obvious outlying data points. As the numerical values obtained from the Freundlich Isotherm may only be considered as indicative, a more sophisticated form of statistical analysis (as undertaken for the kinetic studies) was not pursued. These outlying data points were then eliminated and the remaining results were examined by means of regression analysis.

5.4.2 Freundlich Isotherm - copper, chromium and arsenic

Freundlich Isotherms were successfully constructed for copper adsorption at two of the three

pH values of 5.5, 6.4 and 7.0. The Freundlich isotherm was successful at the pH values of 5.5 and 7.0. Freundlich Isotherms were successfully constructed for chromium and arsenic adsorption at the three pH values of 5.5, 6.4 and 7.0. The graphical constructions are shown below, and subsequently tabulated are, the total number of data points available; the number of data points utilised in the construction; the variance (R squared) between the actual results and the calculated isotherm; the value of the Freundlich equilibrium distribution coefficient (K_F), and the Freundlich power coefficient (M) for each metal at the various pH values.

(a) Copper

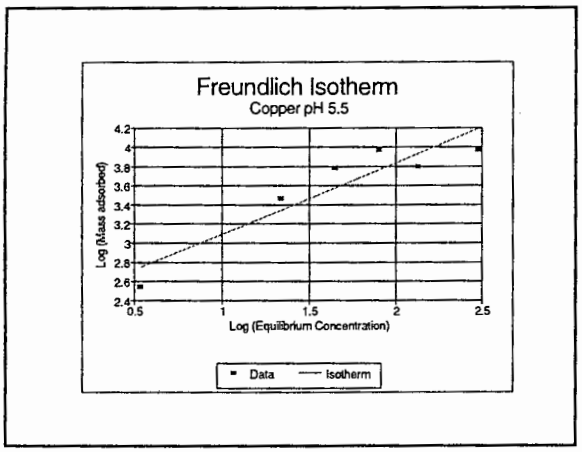

Figure 5.32
Freundlich Isotherm: copper @ pH 5.5

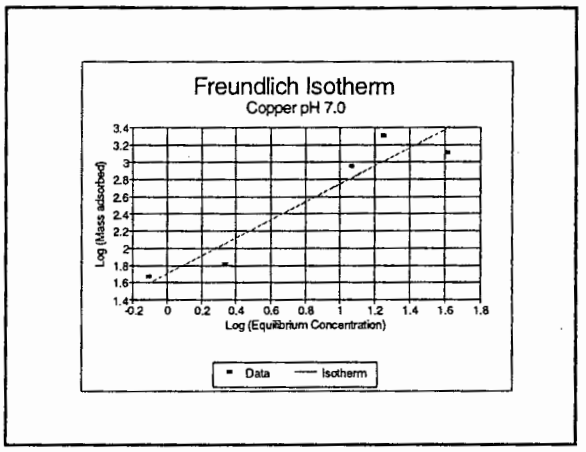

Figure 5.33
Freundlich Isotherm: copper @ pH 7.0

(b) Chromium

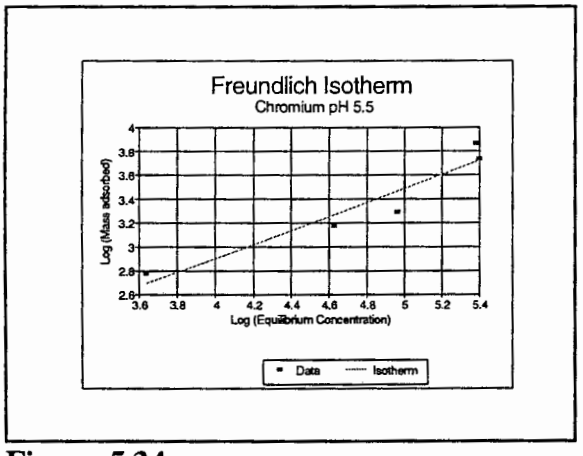

Figure 5.34
Freundlich Isotherm: chromium @ pH 5.5

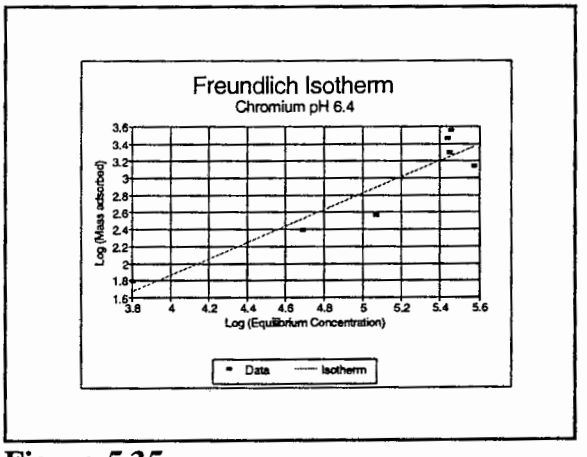

Figure 5.35
Freundlich Isotherm: chromium @ pH 6.4

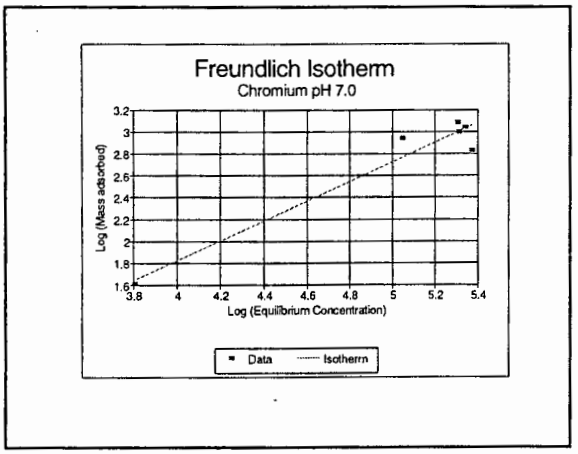

Figure 5.36
Freundlich Isotherm: chromium @ pH 7.0

*(c) **Arsenic***

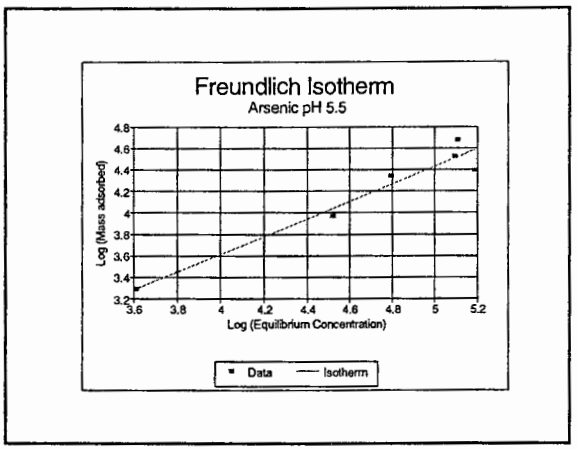

Figure 5.37
Freundlich Isotherm: arsenic @ pH 5.5

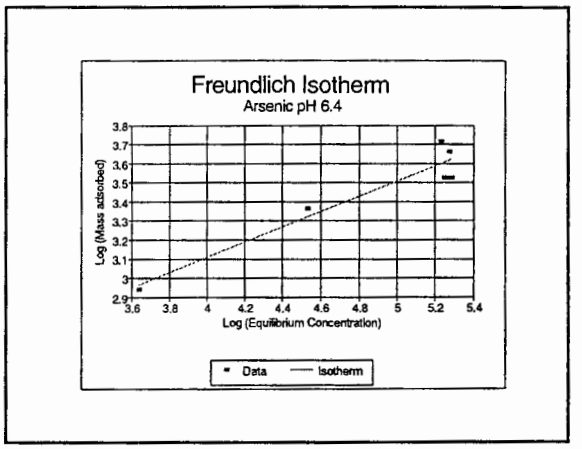

Figure 5.38
Freundlich Isotherm: arsenic @ pH 6.4

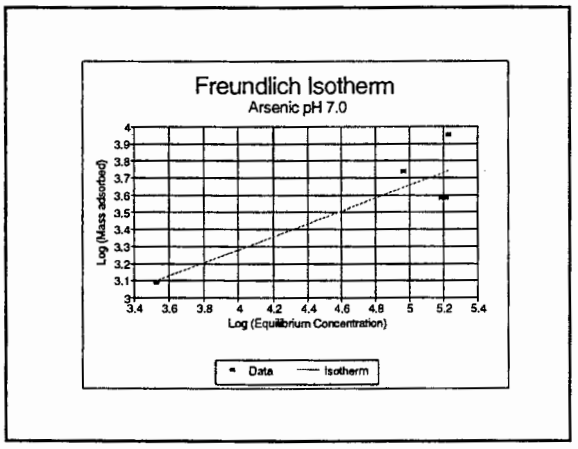

Figure 5.39
Freundlich Isotherm: arsenic @ pH 7.0

Consider Table 5.1 shown below. The variance (R squared) ranged from 0.760 (arsenic at pH7.0) to 0.943 (chromium at pH7.0). As mentioned in section 4.8, copper and chromium analysis could be repeated in some instances. That facility was not available for arsenic. There does not appear to be any physical meaning of the exponent of the concentration term in the Freundlich equation (M) (Kuo *et al*, 1974). Researchers rarely comment on these numerical values, usually only reporting that analytical results conform to one type of adsorption isotherm and quoting the degree of agreement achieved. Therefore, there would not appear to be any great relevance in discussing these numerical values at length.

However, if one considers soils, typically experimental data for the power of the concentration term (M) approximate 1, an example being the adsorption of many pesticides at dilute concentrations (Tan, 1993). It can be seen that the power term for both copper and chromium, conformed to this generalised rule. Arsenic adsorption only conformed at pH5.5. Elkhatib and fellow workers (1984) quote values of M obtained from arsenite (As(III)) adsorption on five West Virginian soils. The values range from 0.399 to 0.958. The calculated results shown in Table 5.1 range from 0.40 to 1.04.

Freundlich equilibrium distribution coefficient (K_F) may be considered as a measure of affinity between solute and adsorbent (Murali *et al*, 1983). The degree of affinity of the metals with municipal solid waste is, copper > arsenic > chromium; a factor of 10 differentiating between the three metals, at pH5.5. At pH6.4, arsenic >> chromium. At pH7.0, copper ≈ arsenic >> chromium.

Table 5.1 Calculated results - Freundlich adsorption isotherms

Metal	pH	Maximum regression observations available	Utilised number of regression observations	R squared	Freundlich equilibrium distribution coefficient (K_F)	Freundlich power coefficient (M)
Copper	5.5	7	6	0.859	0.21	0.74
Copper	7.0	7	5	0.895	0.11	1.04
Chromium	5.5	7	5	0.911	$35E10^{-3}$	0.58
Chromium	6.4	7	7	0.871	$2.8E10^{-3}$	0.96
Chromium	7.0	7	6	0.943	$3.4E10^{-3}$	0.90
Arsenic	5.5	7	6	0.941	$2.8E10^{-2}$	0.82
Arsenic	6.4	7	6	0.915	$9.7E10^{-2}$	0.40
Arsenic	7.0	7	5	0.760	$12E10^{-2}$	0.40

5.4.3 Initial evaluation of adsorption and desorption of copper, chromium and arsenic onto/from municipal solid waste

The results from the kinetic trials were first examined to appraise the degree of variability of the results, the effect of pH, and the degree adsorption and desorption of the metallic ions. The tabulated results are assembled in Appendix F. Graphical representations of adsorption/desorption are shown below (Figures 5.40, 5.41 and 5.42).

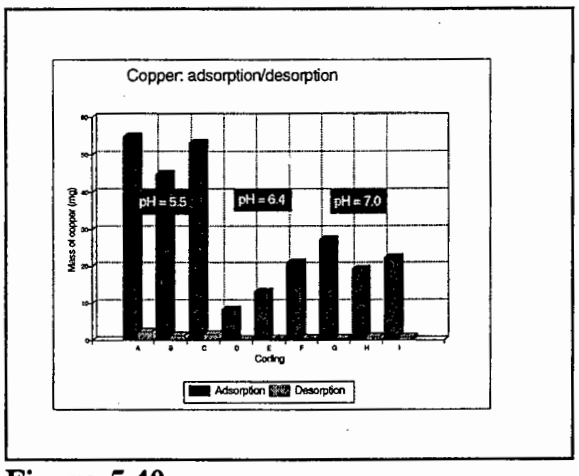

Figure 5.40
Mass of copper adsorped/desorped at pH 5.5, 6,4 and 7.0

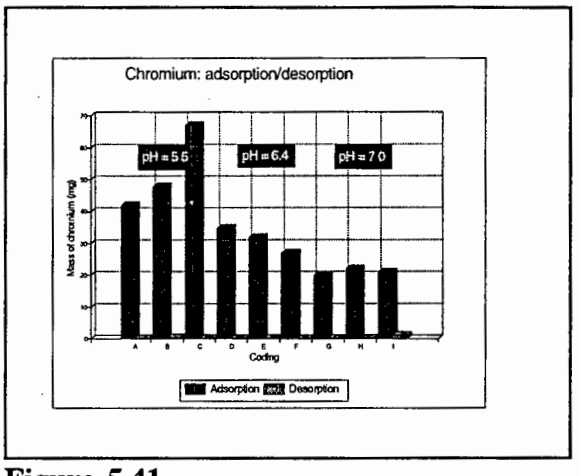

Figure 5.41
Mass of chromium adsorped/desorped at pH 5.5, 6.4 and 7.0

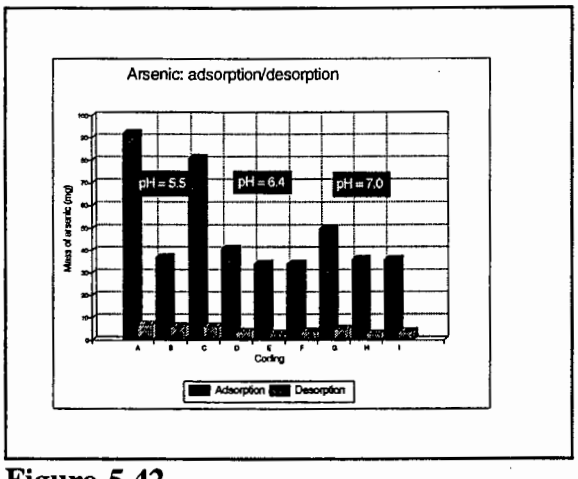

Figure 5.42
Mass of arsenic adsorped/desorped at pH 5.5, 6.4 and 7.0

It can be seen in Figures 5.40, 5.41 and 5.42 there is a degree of variability between samples, especially when considering adsorption. This phenomenon was not unexpected; municipal solid waste is an extremely heterogeneous solid. This was the primary reason that the kinetic experiments were completed in triplicate at the three pH values. In some cases there is, however, a substantial anomaly in results. Considering Figure 5.41, the adsorption of chromium shows a large difference between the three samples designated A, B and C. The initial concentration of chromium in the sample was virtually identical at 263mg (A), 265mg (B) and 263mg (C). Nonetheless, sample C adsorped 67mg of chromium while sample A adsorped 42mg and sample B adsorped 48mg, the latter two exhibiting a similar degree of adsorption. This difference can only be explained by the differing composition of the adsorbent. A similar phenomenon is present in Figure

5.42. The adsorption of arsenic at pH5.5 is extremely variable. There is a large difference between the initial arsenic concentrations but a reversal of the observations regarding chromium. Samples A and C, with widely differing initial concentrations (225mg and 260mg, respectively), show a similar degree of adsorption (92mg and 81mg, respectively). Sample B, with an initial arsenic solution concentration of 231mg, adsorbs only 37mg.

On initial evaluation the effect of pH upon adsorption does not appear significant. Initial solute concentration is the primary variable. Figures 5.43, 5.44 and 5.45 show the effect of initial concentration on mass of solute adsorped. Initial concentration decreases with respect to the y-axis in all three figures. The pH value of that experiment is also shown together with the experimental coding.

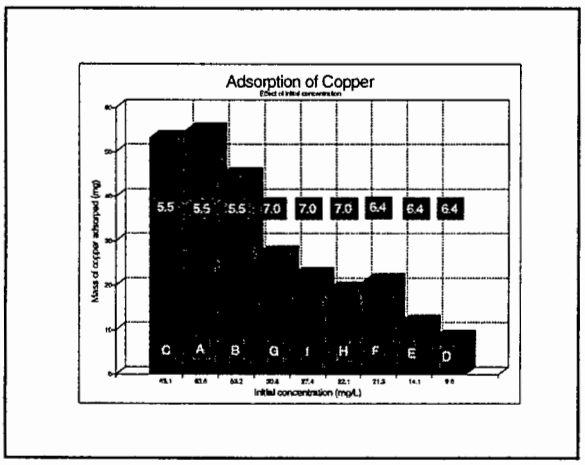

Figure 5.43
Copper adsorption with respect to initial solute concentration

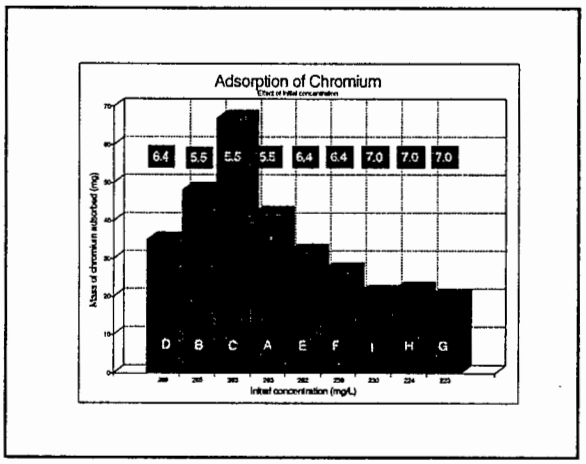

Figure 5.44
Chromium adsorption with respect to initial solute concentration

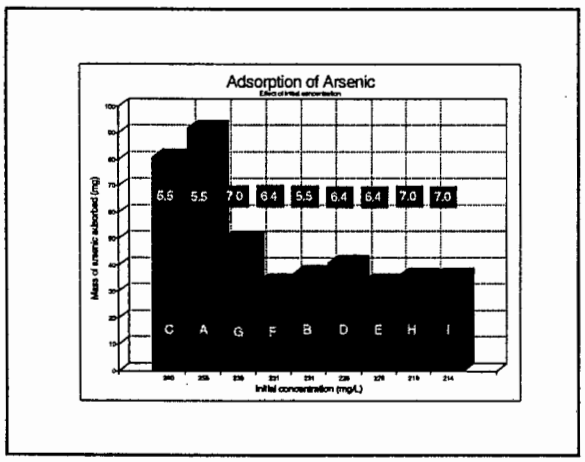

Figure 5.45
Adsorption of arsenic with respect to initial solute concentration

High rates of adsorption occur for copper at low pH levels (Figure 5.43), as a result of the experimental method (section 4.5.1). Before commencement of the kinetic trials the pH of the solution was adjusted, after the addition of the metals to the solution. This allowed any precipitation to occur prior to evaluating adsorption. Therefore, at lower pH levels, higher levels of copper were present, a consequence of solubility constraints. Lower adsorption rates for both chromium and arsenic appear to occur because the initial concentration of those metals was higher at the lower pH level. Again, this may be attributed to the experimental method. When adjusting the pH, precipitating copper entrained both chromium and arsenic, resulting in lower concentrations of copper and arsenic

at time zero of the kinetic trials. This may be seen in Appendix B, Table B-4. In all cases, the original concentration (prior to pH adjustment) of chromium was approximately 270mgℓ^{-1} and between 270 and 280mgℓ^{-1} of arsenic. It may be clearly seen in the figures, the initial concentration of both chromium and arsenic is substantially lower at the higher pH values. The effect of pH upon solute adsorption is further examined in section 6.3.

The table below shows average values of adsorption and desorption at the various pH values for the three metals under consideration.

Table 5.2 Comparison of mass of copper, chromium and arsenic adsorbed and desorbed at pH 5.5, 6.4 and 7.0

Metal	pH	Average Mass sorbed (mg)	Average Mass desorbed (mg)	Percentage of metal adsorped that is desorbed
Copper	5.5	50.9	1.7	3.3
	6.4	14.1	0.5	3.5
	7.0	23.0	0.8	3.5
Chromium	5.5	53	0.2	0.4
	6.4	31	0.2	0.6
	7.0	21	0.5	2.4
Arsenic	5.5	70	6	8.6
	6.4	36	4	11.1
	7.0	41	4	9.8

The desorption of chromium was insignificant, the desorption of copper was less than 4 percent of that adsorped. Arsenic desorption was more significant. It did however, average less than 10 percent of the arsenic adsorped.

Analytical considerations of the method of analysis are of importance when appraising results at relatively low concentrations. The method of arsenic determination employed to analysis of the leachate samples was hydride generation. Hydride generation is an extremely sensitive method, allowing measurement in the parts per billion range. The limit of detection is 2μgℓ^{-1}, accuracy is estimated at approximately 92 percent, within the optimum working range. This method was not available for analysis of the samples taken during the kinetic trials. The only analytical method available was flame atomic adsorption where the optimum working range was 50 - 200mgℓ^{-1} , the sensitivity within the optimum range being 0.78mgℓ^{-1} . This method was suitable for adsorption studies as the samples could be diluted to within the optimum range. However, at low concentrations (such as those experienced in the desorption trials)

the degree of accuracy of the determination of arsenic can only allow the results to be utilised to examine trends. Calculation of kinetic constants from these results would be inaccurate. Levels of desorption were relatively low, especially in the case of copper and chromium, the kinetics of desorption were not investigated further, and attention was limited to the adsorption kinetics.

5.4.4 Kinetics Calculations

The rate of adsorption of all the metals onto the municipal solid waste was initially rapid and decreased with prolonged reaction time. The results from the kinetics experiments were examined extensively. An array of kinetic equations including zero-, first-, second order and fractional power, were examined and found to be unsuccessful in describing the adsorption of the metallic ions on municipal solid waste. Attention was then directed to reversible orders of reaction. These were equally unsuccessful. A two-constant rate equation was found to be effective in describing the rate of metallic ion adsorption. Kuo and Lotse (1974) developed the two-constant equation to study the kinetics of phosphate sorption and desorption on hematite and gibbsite. The kinetic equation was developed by inserting a time-dependent expression into the Freundlich equation. The modified Freundlich equation used, was in the form;

$$q = K_a C_o t^{1/m} \qquad 3.3$$

where,

q	=	metal adsorped per unit weight of solid (mg)
K_a	=	sorption rate coefficient (h^{-1})
C_o	=	initial metal concentration ($mg\ell^{-1}$)
t	=	reaction time (h)
$1/m$	=	constant

The results from the kinetic experiments were analysed in the manner shown below.

(a) Method of Kinetic data examination

Initially, a logarithmic plot of chromium adsorped (mg) versus time (h) was constructed. This logarithmic plot was then examined for any erroneous data points (see section (b) below). Erroneous data points were then eliminated and the remaining results were examined by means of regression analysis. Regression analysis supplied the following information:

Constant, or y-axis intercept of the regression;
R squared, or variance of the model;
X Coefficient (gradient of the linearised data).

Data generated by the regression analysis was then employed as shown.

$$q = K_a C_o t^{1/m}$$

Taking natural logarithms of both sides of the equation

$$\ln(q) = (1/m)\ln(t) + \ln(K_a C_o)$$

Plotting ln(q) versus ln(t):

(1/m)	=	X Coefficient
$\ln(K_a C_o)$	=	Constant, or y-axis intercept of the regression

The value of C_o, the initial concentration of the metal in solution is known, this allows the calculation of the sorption rate coefficient, K_a.

A plot was then prepared of the actual mass of metal sorbed (mg) and the calculated mass sorbed(mg) versus time (h), utilising all of the reported data (i.e. data points were not rejected). This plot allows the visual examination between the experimental data and that calculated from the regression analysis. To determine the degree of agreement between the measured data and the calculated data, the standard error of estimate (SE) was calculated (Steel and Torrie, 1960).

The standard error of estimate is defined as:

$$SE = [\Sigma (C_m - C_c)^2/(n-2)]^{1/2}.$$

Where,

C_m	=	measured metal sorbed by the soil at time, *t*
C_c	=	calculated metal sorbed by the soil at time, *t*
n	=	number of measurements

The lower the SE values the better the particular values calculated for the modified Freundlich equation describe the kinetics of the sorption of the metallic ions.

*(b) **Significance and rejection of experimental data***

The method of data analysis described above, was repeated in an iterative manner. Where any doubt existed regarding the choice of any possible erroneous data points in the initial logarithmic plot, the logarithmic plot was then re-constructed, releasing those of doubt and reinserting those initially disregarded. The SE was then recalculated again using all eight of the data points. This ultimately ensured the minimum value of SE was obtained, and therefore, the best representation of the experimental data.

To illustrate the method of kinetic data the analysis of chromium at pH7.0 is shown below (i.e. Chromium H).

Table 5.3 Adsorption of chromium at pH7.0 (Chromium H)

Time (h)	Chromium concentration ($mg\ell^{-1}$)	Chromium sorbed (mg)	Ln (sorbed)	Ln (Time)
0.0	224	0		
0.5	212	12	2.485	-0.693
1.0	213	11	2.398	0.000
2.0	210	14	2.639	0.693
4.0	213	11	2.398	1.386
8.0	208	16	2.773	2.079
16.0	204	20	2.996	2.773
32.0	202	22	3.091	3.466

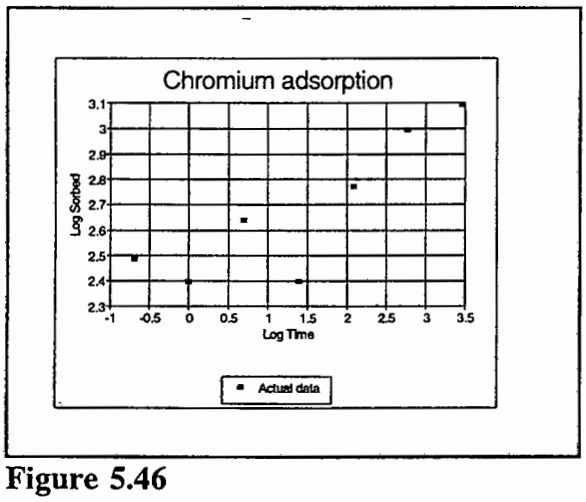

Figure 5.46
Logarithmic plot of measured data: Chromium H

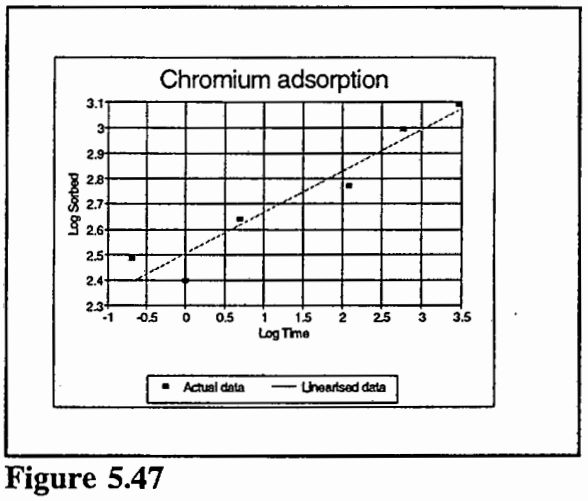

Figure 5.47
Linear regression: Chromium H

Examination of Figure 5.46 it would appear the chromium concentration at time = 4.0h (Log time = 1.386) is erroneous. Examining the remaining results by regression analysis.

Regression Analysis

Constant	=	2.5054
Standard error of Y estimate	=	0.0830
R squared	=	0.928
No. of observations	=	6

Table 5.5 Calculated Results - kinetic experiments

Coding	pH	Initial concentration [C_o] ($mg\ell^{-1}$)	Sorption rate coefficient [K_n] (h^{-1})	Constant [1/m]	Standard Error [SE]
Copper A	5.5	63.6	0.722	0.055	2.93
Copper B	5.5	53.2	0.677	0.063	3.95
Copper C	5.5	65.1	0.668	0.068	2.37
Copper D	6.4	9.6	0.629	0.096	0.92
Copper E	6.4	14.4	0.817	0.061	1.40
Copper F	6.4	21.3	0.766	0.081	1.00
Copper H	7.0	22.1	0.738	0.059	1.02
Copper I	7.0	27.4	0.825	0.064	2.74
Chromium A	5.5	263	0.080	0.182	5.93
Chromium B	5.5	265	0.076	0.237	4.98
Chromium C	5.5	263	0.096	0.243	7.18
Chromium D	6.4	269	0.057	0.252	5.55
Chromium E	6.4	262	0.065	0.152	3.07
Chromium F	6.4	259	0.051	0.189	2.03
Chromium G	7.0	223	0.062	0.099	2.59
Chromium H	7.0	224	0.055	0.162	1.99
Chromium I	7.0	230	0.057	0.162	2.58
Arsenic A	5.5	255	0.199	0.157	5.32
Arsenic C	5.5	260	0.107	0.347	8.84
Arsenic D	6.4	228	0.099	0.166	6.83
Arsenic E	6.4	225	0.096	0.138	10.33
Arsenic F	6.4	231	0.090	0.155	3.77
Arsenic G	7.0	238	0.167	0.089	6.48
Arsenic H	7.0	219	0.090	0.185	3.32
Arsenic I	7.0	214	0.101	0.149	6.38

under the curve must equal unity. The calculated data are assembled in Appendix H, Table H-2; the graphical representations are shown below (Figures 5.49 and 5.50).

The mean of the curve was calculated to be 113.2 days, this is conveniently represented on the **E** curve (Figure 5.50) as "1" on the reduced time x-axis. It can be seen the mean residence time in the column is displaced from the maximum value attained for "**E**". This phenomena is a sure indication of preferential areas of fluid flow (channelling) within the column.

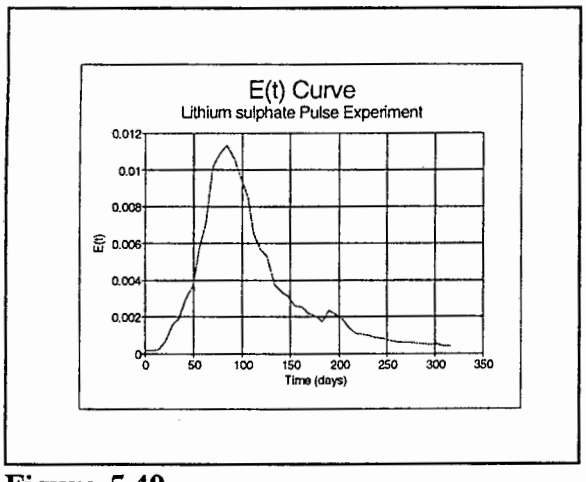

Figure 5.49
E(t) curve: Column 4

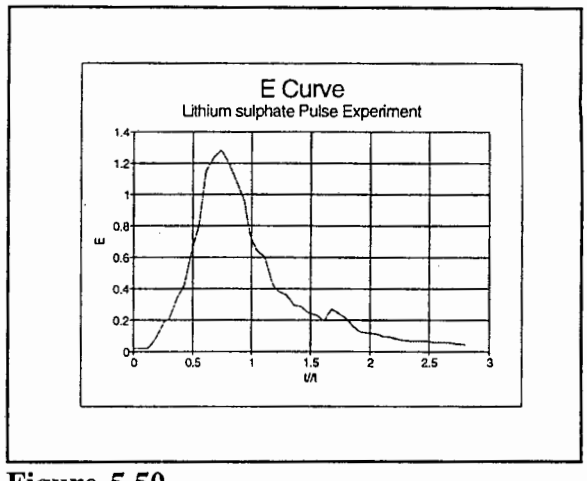

Figure 5.50
E curve: Column 4

The elongation of the base of the curve when compared with the usual thin spike expected for plug flow, is a visual representation of the high value of the variance obtained (σ^2 = 3338). This can be caused by many different flow phenomena, the consequences being either, longitudinal mixing and/or incomplete mixing in the radial direction. A small value of the variance indicates ideal plug flow, the larger the value, the greater the deviation from ideality.

5.4.6 Pilot-scale co-disposal experiment

The calculated results from section 5.4.5, together with the kinetic constants calculated in section 5.4.4 are now employed to calculate the concentration of the three metallic ions in the outlet of the leachate from column 3. The analytical results from columns 3 and 5 are similar, but as the co-disposal experiment was marginally longer for column 3, attention is focused upon that column.

(a) Method of transforming residence time distribution data
The results from the lithium sulphate pulse experiment on column 4 are employed to supply residence time distribution data for column 3. This is a reasonable action as:

(i) the municipal solid waste employed in all the columns is from a common source;
(ii) the municipal solid waste was reduced to the same size range;
(iii) the degree of compaction obtained within the columns is similar for all;
(iv) the height of municipal waste is in the columns is virtually identical;
(v) the process of size reduction "homogenised" the municipal solid waste
(vi) the larger mass of municipal solid waste used in the pilot-scale studies (approximately 700kg) versus the 50g utilised in the laboratory scale experiments should minimise differences between individual columns.

The volumetric displacement of leachate employed during the tracer study (using column 4) averaged $5.21\ell day^{-1}$, whilst the volumetric displacement of leachate through column 3 averaged $2.75\ell day^{-1}$. This difference in volumetric displacement is only a function of the volume of liquid present above field capacity, in the system. However, volumetric displacement of leachate does differ between the two columns and the residence time data from column 4 required mathematical manipulation to realise the conditions in column 3.

Examining the data, a number of methods to achieve this objective were tried. The most successful was to adjust the number of days to correspond with the smaller volumetric displacement obtained from column 3. This was successful, the volume of liquid flowing in the initial increments (i.e. 7 days) remained the same, but the time duration to obtain that volume was proportionally increased to 13.2 days ($7 \times 5.21/2.75$). This transformation was continued for all the data from the lithium pulse experiment. The characteristic curve is then maintained and no further calculation is required. A similar exercise was performed on the data obtained for the calculation of the mean for column 4, and the variance; new values may then be obtained for column 3. The tabulated calculations for the evaluation of the area under the curve, the mean of the curve, and the variance are assembled in Appendix I.

(b) Graphical data

The calculations are shown in Appendix I, Table I-2.

Area under the curve $= \sum m_i \Delta t_i = 12695.7$ mg day

Mean of the curve ($\bar{t}$) $= \sum m_i t_i \Delta t_i / \sum m_i \Delta t_i = 2720477.6/12695.7$

$= 214.3$ days

Variance (σ^2) $= (\sum m_i t_i^2 \Delta t_i / \sum m_i \Delta t_i) - \bar{t}^2$

$= (734706779/12695.7) - (214.3)^2$

$= 11953$

The time taken to displace lithium from the experimental system for the tracer study was 317 days. The total residence time is now calculated to be 600 days ($317 \times 5.21/2.75$).

The transformed graphs are shown overleaf (Figures 5.51, 5.52 & 5.53), the calculations are shown in Appendix I, Table I-1. It can be seen in Figures 5.51 to 5.53, that the method of transformation from the larger volumetric displacement in column 4 to the smaller volumetric displacement in column 3, retains the characteristic curve obtained in the lithium sulphate pulse experiment (Figures 5.28, 5.49 and 5.50). The mathematical transformation extends the base of the curve to accommodate the longer residence time of the lower volumetric displacement.

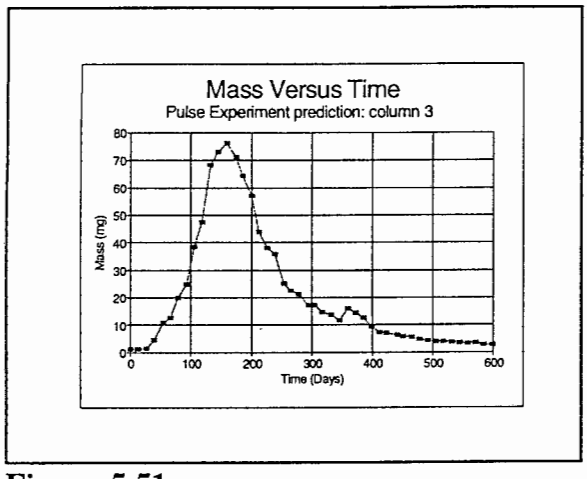

Figure 5.51
Predicted lithium mass versus time relationship for column 3

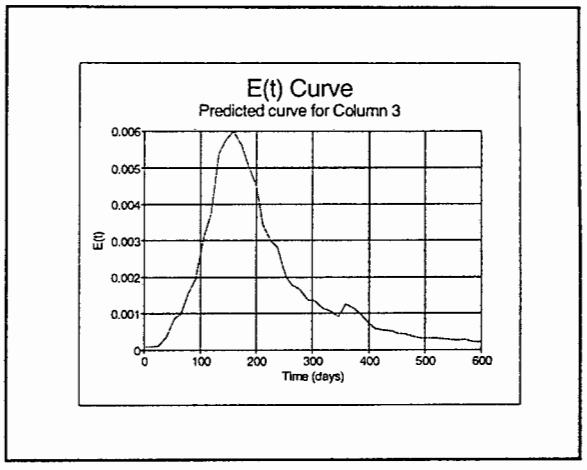

Figure 5.52
Predicted **E**(t) curve for column 3

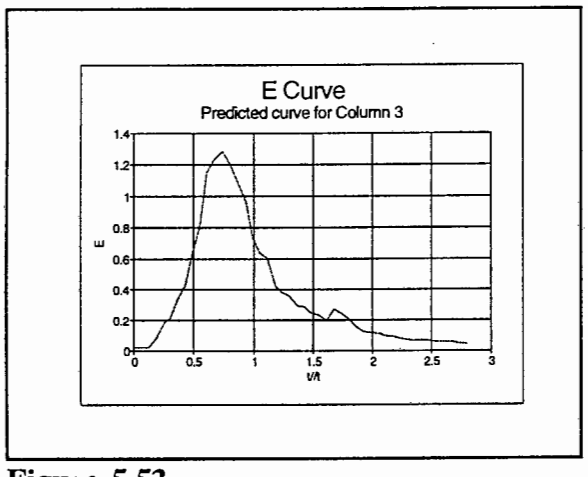

Figure 5.53
Predicted **E** curve for column 3

(c) Calculation of metallic ion concentration in leachate

Two mathematical methods were considered to calculate the concentration of the ions in the liquid effluent from the column. Both use the residence time data as a basis. The **E**(t) curve data allow the calculation of the volume of liquid leaving the column at any time increment during the total time. Both methods are dependent on the manner in which one envisages the liquid to behave in the column. One can view the column as a number of

pipes of differing diameter through which the liquid of differing residence times flow, none of the elements of fluid hinder one another, and any metal adsorped does not affect any subsequent liquid of longer residence time.

Another method, is to consider that all the liquid passes through the column in the same path, leaving in its wake adsorped metal which then reduces the capacity of the adsorbate to adsorb metal contained in liquid elements of longer residence time. This adsorbed metal has to be allowed for in the calculation. It would appear probable, that at short liquid residence times, the first *scenario* is correct, whilst at longer residence times, the latter *scenario* is the more accurate. Both methods of calculation were attempted. It was found that the latter method more accurately predicted the behaviour of the metal content in the leachate to the available data obtained from column 3. Consequently, this method is employed in the subsequent calculations.

The mathematical computation employs a conventional chemical engineering mathematical approach used to solve in the presence of unsteady state conditions (section 3.4.4). The calculation is performed incrementally. This allows for the differing residence time frames, of the various elements of fluid, flowing through the column. Each incremental residence time is overlaid upon the previous shorter residence time until the longest residence time is the last time frame to compute.

As the rate of adsorption is initially rapid and decreases with time, the depth increment must be minimised to ensure the calculation accurately reflects the real situation within the column, where the low residence time elements of fluid flow rapidly and will not reach equilibrium with the solid waste. The depth increment was therefore minimised to 20mm. The time increment was also minimised (to ensure accuracy was maximised), to the minimum possible provided by the experimental procedure, approximately 13 days.

The method adopted for the formulation of the copper-chromium-arsenic solution at the various pH values made allowance for precipitation at the relevant pH (section 4.5.1). The solution employed during the kinetic trials was first formulated at a low pH, adjusted to the relevant pH by use of sodium hydroxide. Precipitation was then allowed to occur. The initial values of the kinetic trials were the maximum concentration of the metal that would occur at that pH. When the combined copper-chromium-arsenic solution was prepared in the laboratory, there was a substantial reduction of the mass of copper in solution from approximately $80mg\ell^{-1}$ to $22mg\ell^{-1}$ due to precipitation. It would appear, that although 88.4g of copper are added, virtually all of this copper would precipitate upon introduction into the column.

With a full scale landfill, water can come only from three sources; moisture provided by a precipitation event (rainwater); moisture from deposited solid waste, and moisture produced from anaerobic activity. The major source of moisture is rain water. Rainwater has a negligible alkalinity content and therefore would not raise the pH of the copper-chromium-arsenic solution. Precipitation of copper would not occur, unless the rainwater was able to mobilise alkaline constituents, within the landfill. When water is in contact with stabilised municipal solid waste, very high levels of alkalinity can be observed. This is evident in the results quoted in this chapter, where the alkalinity approximated

4000mgℓ^{-1} (section 5.3.1). It may be concluded that virtually all the copper deposited with municipal solid waste would precipitate as copper hydroxide at or near proximity to its place of deposition. Analytical results confirm these statements.

Extremely low levels of copper were detected in the leachate from columns 3 and 5. Copper concentration in the leachate from column 3 did not exceed 0.11mgℓ^{-1}. Over the entire period of monitoring (235 days), the concentration of copper in the leachate from column 3 averaged 0.05mgℓ^{-1}, i.e. no higher than the initial reading at Day zero. The initial concentration of copper in the leachate from column 5 was 0.07mgℓ^{-1}. This value was not exceeded for the entire duration of the experiment. The final copper concentration after 221 days was 0.04mgℓ^{-1}. Over the entire period of monitoring (221 days), the concentration of copper in the leachate from column 3 averaged 0.03mgℓ^{-1}. For these reasons, the calculation of copper content was not computed.

The computation to predict chromium concentration employed the results obtained from the laboratory scale kinetic trail designated "chromium H". This outcome of this trial was the lowest standard error of the three trials at pH7.0 (1.99), the approximate pH of leachate exiting the pilot-scale columns. The values employed are:

K_a	=	sorption rate coefficient (day^{-1})	=	0.092
1/m	=	constant	=	0.162
Maximum sorption	=	21mg per 50g adsorbate	=	0.42gkg^{-1}

The calculation is shown in Appendix J. The predicted concentration of chromium over the total time period of 600 days (Figure 5.54) is extremely interesting, dispelling commonly held views.

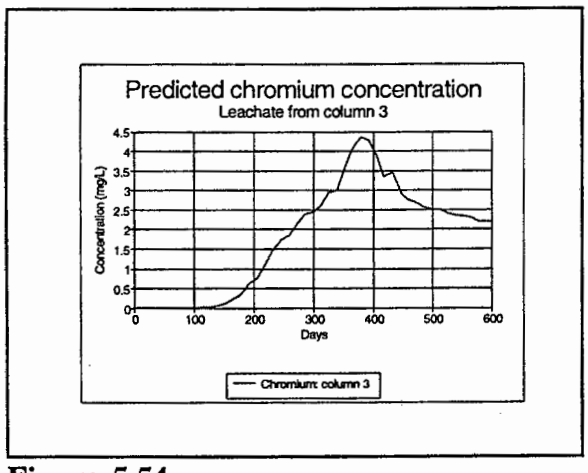

Figure 5.54
Predicted concentration of chromium in leachate from column 3

One would anticipate chromium concentration in the leachate to be initially high, as hydrodynamic factors such as fluid channelling and by-passing would convey chromium through the adsorbent. This does not occur, and the column behaves as a plug flow reactor, albeit a reactor with high degree of non-ideality. The maximum chromium concentration occurs on Day 390 at 4.4mgℓ^{-1} The secondary peak occurring at approximately Day 430 is a product of the smaller secondary peak which occurred in lithium pulse experiment.

For graphical scalar considerations, two figures are presented to illustrate the predictions of the computed model and that achieved in practice. Figure 5.55 shows predicted and actual results until Day 194; Figure

5.56 shows results until cessation of monitoring on Day 235. Considering Figure 5.55, until Day 142 the model realises actual measurements well, with very little deviation. From Day 142 the model begins to overpredict actual conditions. Results from monitoring continue in the region of $0.03mg\ell^{-1}$ whereas the model begins to predict chromium concentrations in excess of $2mg\ell^{-1}$ (Figure 5.56) in that time frame.

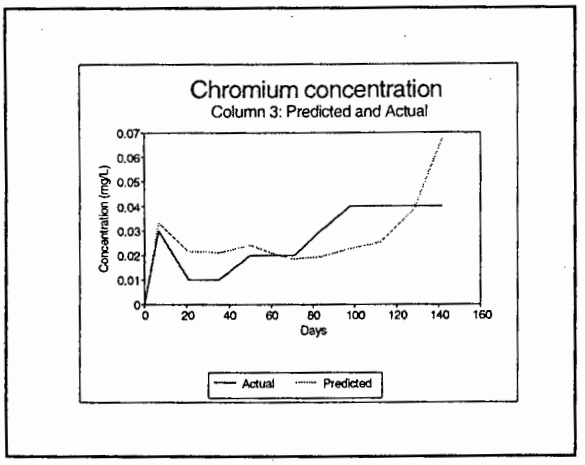

Figure 5.55
Predicted and actual concentration of chromium in leachate from column 3 until day 142

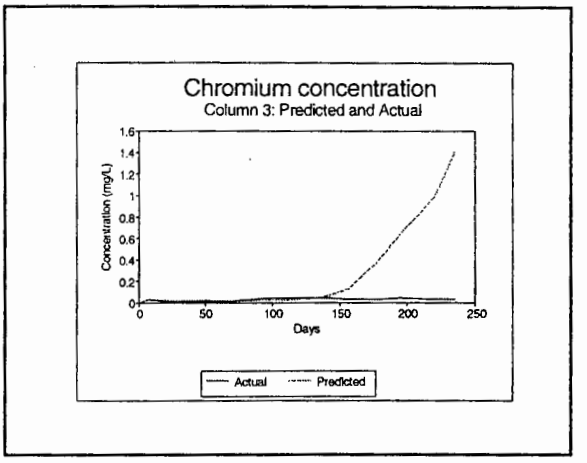

Figure 5.56
Predicted and actual concentration of chromium in leachate from column 3 until day 234

There are three obvious factors to consider:

(i) the affinity for chromium exhibited the solid waste in the pilot-scale landfill columns was not realised in the kinetic trials;

(ii) the method of computation does not model conditions in the pilot-scale columns with sufficient accuracy;

(iii) the transposing of the information obtained from the tracer studies undertaken on column 4 to column 3 could not be supported in practice.

The deviation of predicted values from that achieved in practice is only exhibited after a relatively long period of time has elapsed (160 days). It is therefore unlikely, that comments (ii) and (iii) are the major contributory factor. It is probable that factor (i) is appropriate. Soil science researchers, Bartlett and James (1988) document similar occurrences. The drying and storage of soils can alter the surface characteristics of that soil. If this is applicable to soils, a similar analogy can be drawn from municipal solid waste. Another additional factor is the sample size utilised in the kinetic experiments. Only 50g was used, while the pilot-scale columns where packed with approximately 700kg of municipal solid waste. While sampling was exhaustive, solid waste is an extremely heterogeneous substance.

The predicted arsenic concentration employed the results obtained from the laboratory scale kinetic trial designated "arsenic H". This outcome of this trial was the lowest standard error of the three trials at pH7.0 (SE = 3.32), the approximate pH of leachate exiting the pilot-scale columns. The values employed are:

K_a	=	sorption rate coefficient (day^{-1})	=	0.090
1/m	=	constant	=	0.185
Maximum sorption	=	36mg per 50g adsorbate	=	$0.72gkg^{-1}$

The predicted outcome of the co-disposal of arsenic was calculated in the same manner as that of chromium. Calculations predicted there would be an absence of arsenic in the leachate from column 3 during the total time period of 600 days. The results quoted in section 5.3.3(c) showed a maximum arsenical content of the leachate of approximately $2mg\ell^{-1}$. The results from desorption kinetic trials (section 5.4.3, Table 5.2) showed that arsenic was the only metal of those under consideration that displayed any significant degree of desorption. This could not be allowed for in the calculation, and could account for the extremely low degree of error that is evident.

The method of computation allowed the graphical representation of the results in terms of metal saturation with depth and time. These are shown below in Figures 5.57 and 5.58.

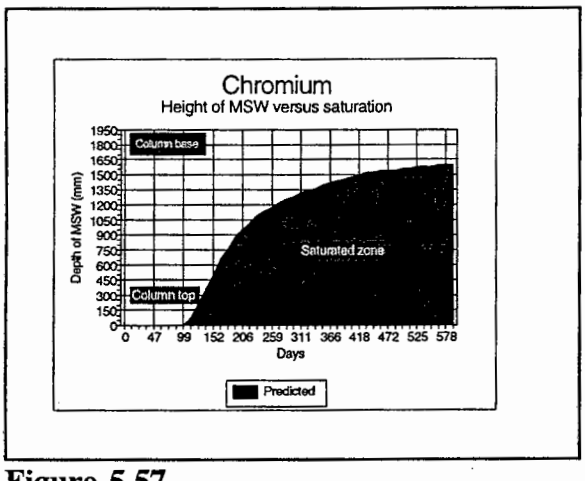

Figure 5.57
Chromium saturation versus column depth

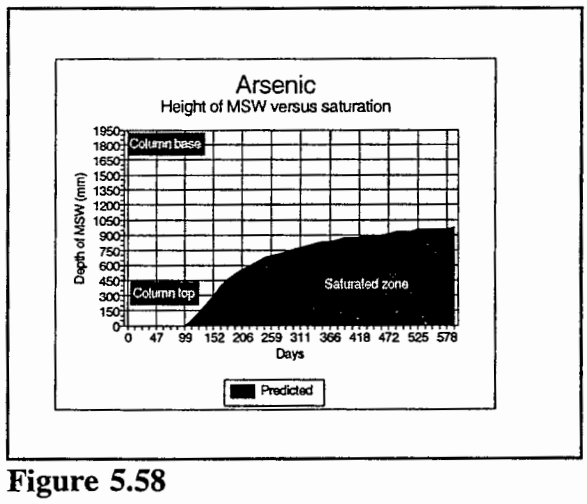

Figure 5.58
Arsenic saturation versus depth

After 99 days, both metals started to reach their equilibrium maximum value in the initial 20mm of municipal solid waste. The total height of municipal solid waste in column 3 was 1 940mm. Chromium almost completely saturated the column over the 600 day period. Further addition of chromium would result in high levels of chromium in leachate. The mass of chromium added to the column was 256.1g. The degree of column saturation, is a consequence of the low maximum chromium equilibrium value of 0.42g of chromium per kilogram of municipal solid waste. The final depth of saturation for chromium was 1 600mm. The mass of arsenic added was 256.7g. The degree of arsenic saturation is far less than that of chromium reaching only 980mm, approximately half the

column depth. The equilibrium saturation concentration is high in comparison with the other metals under consideration, at 0.72gkg^{-1}. These graphical representations indicate the importance of the maximum saturation value. The rate of reaction is not dissimilar between chromium and arsenic. However, the high affinity of arsenic for the municipal solid waste results in far less mobility within the column. The mean residence time in the column was computed to be 214 days, at that time chromium had saturated the waste in the column to a depth of 1 020mm, and arsenic to a depth of 600mm.

Analytical results for all the metals under consideration are available only for comparison for the first 235 days of an anticipated 600 day residence time period. In this 235 day time frame the modelled results are an excellent response to that experienced at pilot-scale. The results for copper cannot be compared as precipitation occurs. Both chromium and arsenic analytical results compare vary favourably with that predicted. There are additional factors to consider. These are discussed in Chapter 6.

5.4.7. Application of the pilot-scale studies to the full scale landfill

In this sub-section the results obtained at pilot-scale are utilised to provide functional data that may be applied by the landfill practitioner. It was decided to employ a worst-case study. The assumptions of this worst-case study are detailed below.

(i) Precipitation occurring in the heaviest precipitation month proceeded to fall on a continual basis;
(ii) no loss of moisture from the landfill, such as evapotransportation or run-off;
(iii) the landfill was at field capacity prior to co-disposal;
(iv) metal content in leachate from the landfill should not exceed the most stringent requirements prescribed by current South African legislation.

The municipal solid waste utilised in this study was excavated from Coastal Park Sanitary Landfill Site (section 4.3). Therefore, to continue with a site-specific study, detailed precipitation data was available and was obtained for the Coastal Park Sanitary Landfill Site for the period 1991 to 1994 (City of Cape Town, 1994). During this period the greatest amount of precipitation occurred during June 1994. Rainfall approximated 290mm. In South Africa, the quality of water discharged into a catchment, where water in that catchment area will be subsequently purified to drinking water quality, is determined by The Water Act, 1956 (Act No. 54 of 1956) (DWA, 1956). The Water Act was originally promulgated in 1956, though there have been many subsequent amendments. The Special Standard (DEAF, 1984) defines the requirements of wastewater or effluent draining into a catchment area. The maximum allowable concentration of copper is 0.02mgℓ^{-1}; the maximum allowable concentration of chromium is 0.05mgℓ^{-1}; the maximum allowable concentration of arsenic is 0.1mgℓ^{-1}.

As shown in section 5.4.6(c), predicted chromium concentration in the leachate from column 3 exceeded analytical measurements (4.4mgℓ^{-1} *versus* 0.03mgℓ^{-1}). Conversely, predicted arsenic concentration in the leachate from column 3 was exceeded by analytical measurements (zero *versus* 2mgℓ^{-1}). It would appear reasonable to assume, if predicted chromium concentration is reduced to a maximum of 0.05mgℓ^{-1}, actual concentration in

arsenic in leachate would approximate zero. Attention is therefore focused on leachate chromium concentration.

Firstly, precipitation data were transposed into leachate volumetric displacement.

Maximum rainfall	=	290mm (June 1994)
Landfill column, cross-sectional area	=	$0.25 \times \pi \times 0.7^2$
	=	$0.3848m^2$
Volumetric flow	=	$0.29 \times 0.3848 \times 1000/30$
	=	$3.73\ell day^{-1}$

The residence time data obtained from the tracer studies (section 5.3.2) was then transformed in the same manner as reported in section 5.4.6(a). The same exercise was executed for the calculation of mean of the curve and the variance. The transformed graphs are shown below (Figures 5.59; 5.60 and 5.61) together with the calculated values for the mean and variance.

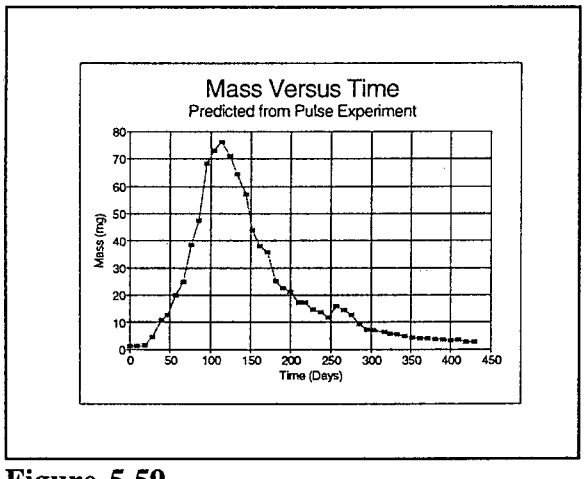

Figure 5.59
Predicted lithium mass versus time relationship: $3.73\ell day^{-1}$

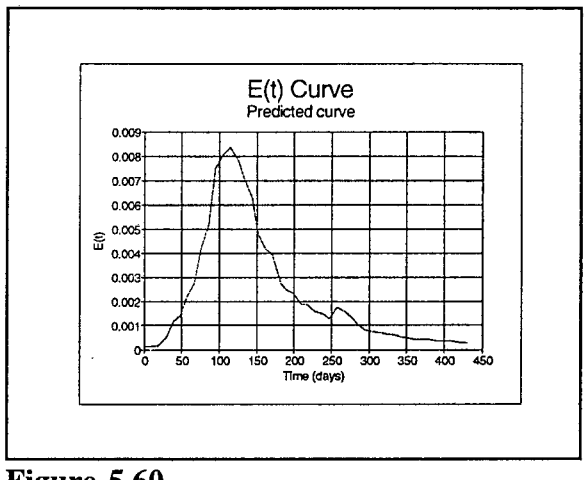

Figure 5.60
Predicted **E**(t) relationship: $3.73\ell day^{-1}$

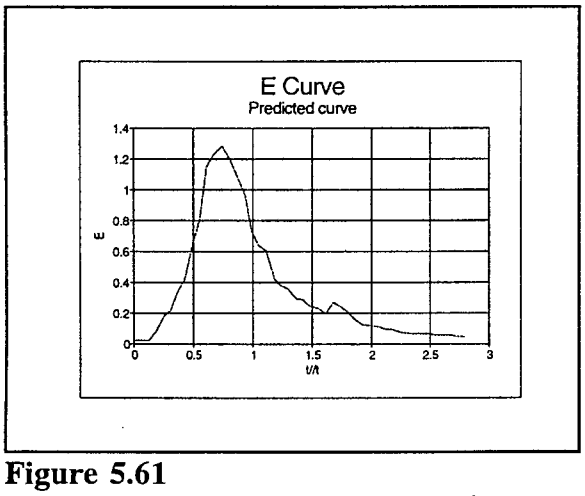

Figure 5.61
Predicted **E** relationship: $3.73\ell day^{-1}$

Mean of the curve ($\bar{t}$) = 153.4days
Variance (σ^2) = 6123

The total residence time for the pilot-scale column at a displacement rate of leachate of $3.73\ell day^{-1}$ is 430 days.

The computation to predict chromium concentration in leachate employed the same numerical values utilised in 5.4.6(c). The initial mass of chromium co-disposed at pilot-scale in column 3 was 256g. The

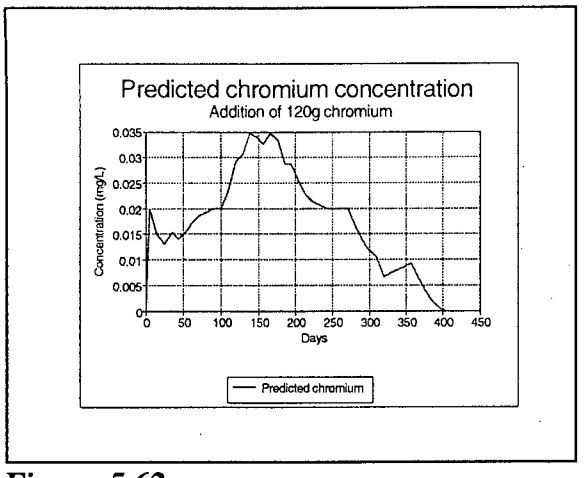

Figure 5.62
Predicted chromium concentration: Assumed addition of 120g of chromium

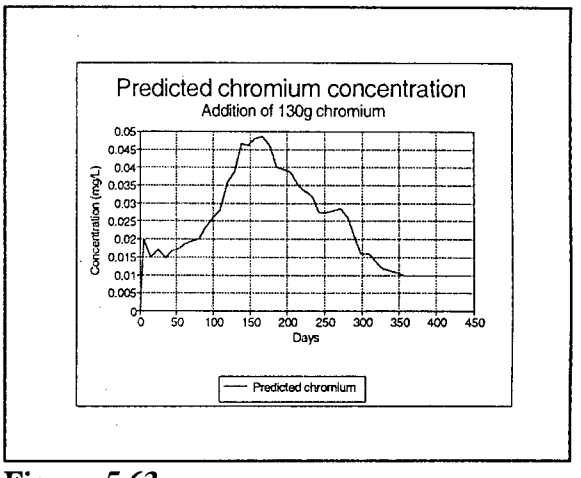

Figure 5.63
Predicted chromium concentration: Assumed addition of 130g of chromium

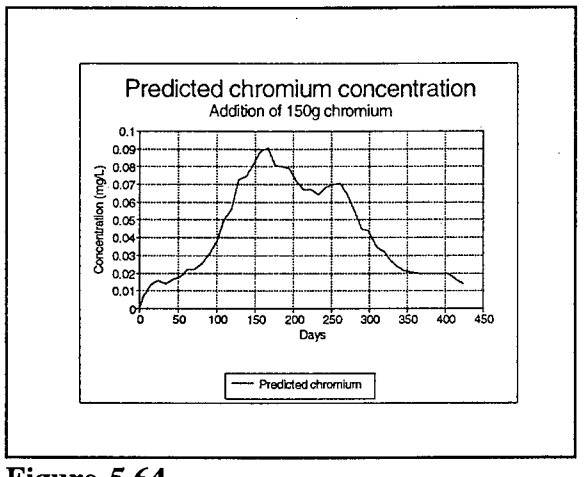

Figure 5.64
Predicted chromium concentration: Assumed addition of 150g of chromium

predicted maximum chromium concentration in leachate was then 4.4mgℓ^{-1}. Therefore, to have a predicted chromium concentration of 0.05mgℓ^{-1} in the leachate, the mass of chromium would have to be far less than 256g. Three modelled calculations were completed; 100g; 120g, and 150g of chromium, being assumed to be added to the column. The graphical representations are shown (Figures 5.62; 5.63 and 5.64). It can be seen that, with the assumed addition of 150g of chromium, predicted leachate chromium concentration reaches a maximum of 0.09mgℓ^{-1} (Figure 5.64) at Day 165. This exceeds the maximum allowable concentration of chromium of 0.05mgℓ^{-1}. With the assumed addition of 100g of chromium, predicted leachate chromium concentration reaches a maximum of 0.035mgℓ^{-1} (Figure 5.62) at Day 165. This concentration is within acceptable limits, but there is sufficient tolerance to add additional chromium. It can be seen from Figure 5.63 the assumed addition of 130g of chromium would result in a predicted chromium concentration of 0.048mgℓ^{-1}. Any further addition of chromium would result in the predicted concentration exceeding the maximum allowable chromium concentration of 0.05mgℓ^{-1}.

The mass of municipal solid waste contained in column 3 was 668kg. The maximum amount of chromium that could be co-disposed with acceptable risk of environmental damage is therefore 195gtonne^{-1}. This chromium would be co-disposed with the proportional amount of arsenic and chromium, as dictated by the composition of the CCA solution. The laboratory scale equilibrium and kinetic studies and the pilot-scale co-disposal trials were conducted with the CCA solution. The CCA (Tanalith) solution has

been characterised fully in section 4.4.1. The ratio of copper: chromium: arsenic is 1 : 2.9 : 2.9. Therefore, if 195g of chromium were co-disposed with municipal solid waste, there would be 195g of arsenic and 67g of copper associated with that amount of chromium.

5.5 SUMMARY

Adsorption equilibrium studies and kinetic studies were undertaken at laboratory scale, at three pH values; pH5.5, pH6.4, and pH7.0. The adsorbent being municipal solid waste, the adsorbate being copper, chromium and arsenic in aqueous solution. Data obtained at equilibrium was successfully described by the Freundlich Isotherm (section 5.4.2).

The kinetic studies revealed a reaction characterised by an initial rapid adsorption rate, the rate of adsorption subsequently decreasing at larger values of time. This reaction could be successfully described by a modification of the Freundlich equation (section 5.4.4) usually termed, the modified Freundlich equation, or the two-constant equation. The modified Freundlich equation was developed by Kuo and Lotse in 1974.

Tracer studies were undertaken at pilot-scale. The tracer employed was lithium sulphate. Tracer studies revealed (as expected) a system with conformed with a plug flow reactor, albeit with a great deal of non-ideality. Co-disposal experiments were then undertaken at pilot-scale. A solution of copper-chromium-arsenic was added to two of the pilot-scale columns. The effluent from the columns was closely monitored. Conventional chemical engineering reactor design allows the computation of reactor effluent composition from results from tracer studies in combination with kinetic results, together with details of the reactor feed.

The pen-ultimate phase of the investigation comprised of a comparison of the results obtained at pilot-scale with that predicted from the laboratory scale studies. Agreement was good between results obtained at pilot-scale with results predicted from the laboratory scale studies. Predicted chromium concentration in the leachate from column 3 exceeded analytical measurements ($4.4 mg\ell^{-1}$ *versus* $0.03 mg\ell^{-1}$). Actual arsenic concentration in the leachate from column 3 exceeded that predicted ($2 mg\ell^{-1}$ *versus* zero) (section 5.4.6(c)).

The final phase of the project employed the model developed from the laboratory scale results to compute the mass of copper-chromium-arsenic solution that could be added to municipal solid waste. A worst-case study was examined (section 5.4.7). Computation showed it is possible to co-dispose 195g of chromium together with 195g of arsenic and 67g of copper per tonne of municipal solid waste with the minimum of environmental damage to any receiving water body.

CHAPTER 6
DISCUSSION

6.1 INTRODUCTION

The results and subsequent calculations generated by the experimental study are examined and discussed in this chapter. The speciation and physical characteristics of the metals are scrutinised. The laboratory scale equilibrium and kinetic studies are examined and a sorption mechanism is proposed. The pilot-scale tracer studies and co-disposal trials are assessed and discussed. The computational method developed to model the pilot-scale studies is appraised and any deficiencies uncovered. The results established at pilot-scale, are applied to the full scale landfill. The effect of the co-disposal of copper, chromium and arsenic in an acetogenic, methanogenic and stabilised landfill assessed.

6.2 SPECIATION OF THE METALS PRESENT IN THE EQUILIBRIUM AND KINETIC TRIALS

It is advantageous to discuss firstly the speciation and the copper, chromium and arsenic under prevailing conditions. Chromium from the CCA wood preservative is present in the form of Chromium(VI), arsenic is in the form of arsenic(V) and copper is in the form of copper(II). Ionic equilibria for copper, chromium and arsenic in an aqueous solution are detailed below, together with their ionic structure in an aqueous medium.

6.2.1 Copper(II)

The Cu^{2+} ion, at ordinary concentrations, begins to hydrolyse above pH4, and precipitation as the oxide (Cu_2O) or the hydroxide ($Cu(OH)_2$) begins soon after. The hydrated ion has the formula $Cu(H_2O)_6^{2+}$ and has a distorted octahedral structure (Jahn-Teller effect). This is a consequence of its d^9 configuration (Nicholls, 1974). Two of the water molecules are in the trans position, these are further removed from the Cu^{2+} ion than the other four, which are coplanar (Cotton *et al*, 1972). The ionic radii of the copper ion in aqueous solution is 0.87Å. The bond lengths are 1.94Å for the coplanar bonds and 2.4Å for the trans bonding ions (Burgess, 1988). It is important to note that copper is present in aqueous solutions in the form of a cation.

Structural details of the hydrated copper ion are shown in Figure 6.1.

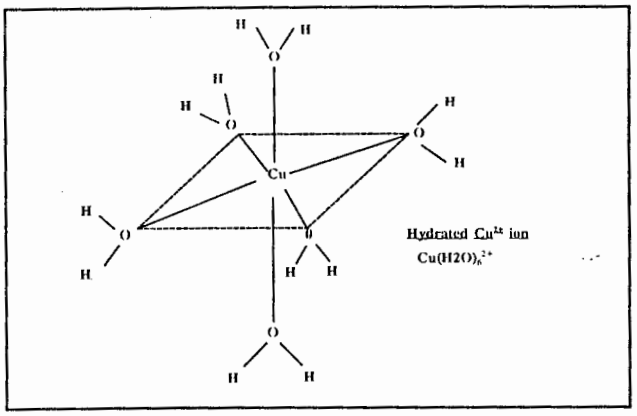

Figure 6.1
Structural details of the hydrated copper ion

6.2.2 Chromium(VI)

Chromium(VI) hydrolyses extensively, so only neutral or anionic species occur in water. The speciation, well established by extensive data are $HCrO_4^-$, CrO_4^{2-} , and $Cr_2O_7^{2-}$. However $Cr_2O_7^{2-}$ is only dominant at chromium(VI) concentrations above 0.01M, in acidic media (Bates *et al*, 1976).

The equilibria for chromium(VI) in aqueous solutions is shown below

$$H_2CrO_4 + H_2O \rightleftarrows HCrO_4^- + H_3O^+ \quad pK_a = 0.74$$

$$HCrO_4^- + H_2O \rightleftarrows CrO_4^{2-} + H_3O^+ \quad pK_a = 6.49$$

CrO_4^- (monohydrogen chromate ion) is the predominant species between pH0.75 and pH6.45, while CrO_4^{2-} (chromate ion) predominates at pH values greater than 6.45. The chromate ion has a tetrahedral structure, with four oxygen atoms bound to a central chromium atom. The mutual repulsion of the four electron clouds direct the oxygen atoms to the corners of an inscribed tetrahedron. Therefore, the monohydrogen chromate ion would have a distorted tetrahedron structure. The ionic radii of the chromium(VI) ion in aqueous solution is approximately 0.63Å. Structural details of the chromate ion are shown in Figure 6.2.

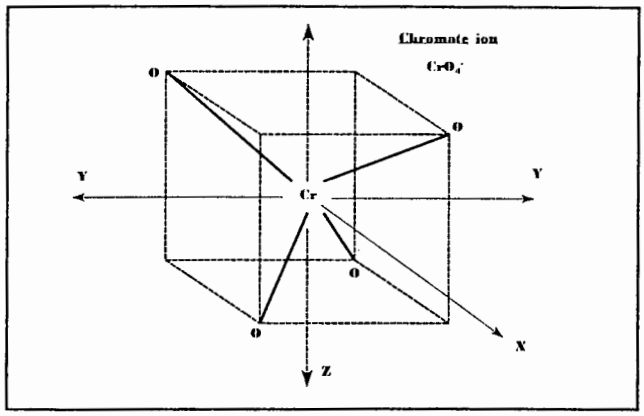

Figure 6.2
Structural details of the chromate ion

Metal to oxygen distances for metal ions in aqueous solutions parallel those obtained for crystal ionic radii and are very similar to those reported for analogous crystal hydrates (Burgess, 1988). This information is relevant. It is difficult to obtain bond lengths for every metal in combination with oxygen in aqueous solutions. The bond length quoted for Cr(III) in aqueous solution by Burgess (1988) is 1.94Å (X-ray diffraction), 1.98Å (EXAFS) and for a crystal hydrate 2.02Å. Wells (1975) quotes the following:

Table 6.1 Bond length: chromium(III) and chromium(VI)

Cr(III) and Cr(VI)	Cr^{III}- 6O (Å)	Cr^{VI}- 4O (Å)
Cr_5O_{12}	1.97	1.65
KCr_3O_8	1.97	1.60
$LiCr_3O_8$	2.05	1.66
$CsCrO_8$	1.96	1.63

It would appear reasonable to estimate the chromium-oxygen bond length in aqueous solution to approximate 1.63Å.

6.2.3 Arsenic(V)

Arsenic(V) in aqueous solution forms an oxyacid whose properties closely resemble dissolved phosphorous(V), which forms H_3PO_4. The dissociation constants and hence their dissociation equilibria are extremely similar. The structure of both phosphoric and arsenic acid is better represented by formulas of the type $MO(OH)_2$.

The equilibria for arsenic acid (arsenic(V)) is aqueous solutions is shown below.

$$H_3AsO_4 + H_2O \rightleftarrows H_2AsO_4^- + H_3O^+ \quad pK_a = 2.25$$

$$H_2AsO_4^- + H_2O \rightleftarrows H_2AsO_4^{2-} + H_3O^+ \quad pK_a = 6.77$$

$$HAsO_4^{2-} + H_2O \rightleftarrows AsO_4^{3-} + H_3O^+ \quad pK_a = 11.60$$

$H_2AsO_4^-$ (mono-ortho-arsenate ion) is the predominant species for pH values from 3.6 to 7.3, whereafter $HAsO_4^{2-}$ (di-ortho-arsenate ion) predominates. Arsenic achieves simple tetrahedral structures in the arsenate ion (Cartmell *et al*, 1961) by use of its sp^3 hybrid orbitals. The mutual repulsion of the four electron clouds direct the oxygen atoms to the corners of an inscribed tetrahedron (Toon *et al*, 1973). Therefore, the mono-ortho-arsenate ion and the di-ortho-arsenate ion would have a distorted tetrahedron structure. The ionic radii of the arsenic(V) ion, in aqueous solution, is approximately 0.70Å. Structural details of the arsenate ion are shown in Figure 6.3.

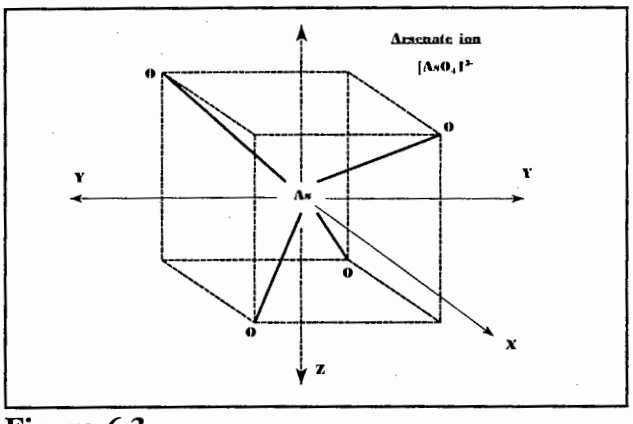

Figure 6.3
Structural details of the arsenate ion

For similar reasons to chromium(VI), the bond lengths relevant to the arsenate ion were not readily available. However, $HAsO_4^-$ has been studied in $(NH_4)HAsO_4$ and $Na_2HAsO_4.7H_2O$ and the bond lengths are As-O; 1.67Å and As-OH; 1.74Å (Wells, 1975).

6.3 ADSORPTION ISOTHERMS

The results obtained from the equilibrium studies were successfully described by the Freundlich isotherm. The Freundlich isotherm results from a consideration of the heterogeneity of the surface, when applied to the adsorption of vapours onto solid surfaces. If adsorption data fit the equation, it is possible, but not proven, that the surface is heterogeneous (Adamson, 1982). If one considers the adsorbent being municipal solid waste there would appear to little doubt the surface is heterogeneous, and the suitability of the Freundlich isotherm, in this instance, is acceptable.

The numerical values of the constants, in addition to the degree of agreement or variance are shown in Table 6.2 below. The variance (R squared) ranged from 0.760 (arsenic at pH7.0) to 0.943 (chromium at pH7.0). As reported in section 4.8, copper and chromium analysis could be repeated in some instances. That facility was not available for arsenic. This could have affected the value obtained for the variance. As previously mentioned in section 5.4.2, numerical values obtained for the Freundlich constants do not appear to be of great value, and their significance was briefly discussed in that section. They do appear useful for the determination of trends, such as the degree of affinity for a solute for an adsorbent, this is discussed below.

Table 6.2 Calculated results - Freundlich adsorption isotherms

Metal	pH	R squared	Freundlich equilibrium distribution coefficient (K_F)	Freundlich power coefficient (M)
Copper	5.5	0.859	0.21	0.74
Copper	7.0	0.895	0.11	1.04
Chromium	5.5	0.911	$35E10^{-3}$	0.58
Chromium	6.4	0.871	$2.8E10^{-3}$	0.96
Chromium	7.0	0.943	$3.4E10^{-3}$	0.90
Arsenic	5.5	0.941	$2.8E10^{-2}$	0.82
Arsenic	6.4	0.915	$9.7E10^{-2}$	0.40
Arsenic	7.0	0.760	$12E10^{-2}$	0.40

Other forms of isotherms were examined and found unsuitable. However, detailed analysis of the equilibrium data revealed a very strong relationship between initial solute concentration in solution and final solute concentration in solution, irrespective of pH. This is displayed graphically below (Figures 6.4, 6.5 and 6.6).

The degree of agreement for this form of representation was surprising; regression analysis supplied the variance (R squared) and the X coefficient (gradient of the linearised data). These calculated values are shown below in Table 6.3. This form of relationship is not uncommon. The value obtained for the X coefficient allows direct calculation of the

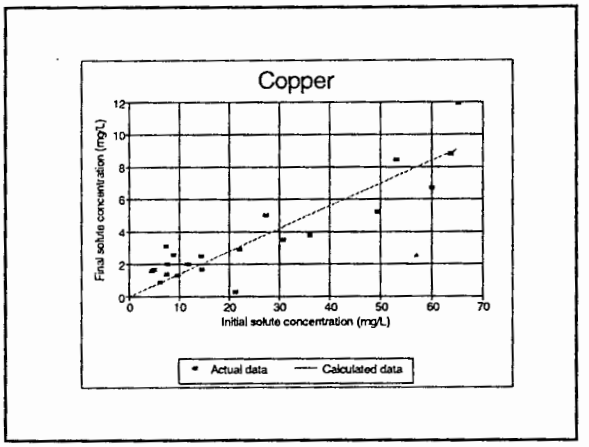

Figure 6.4
Copper: relationship between initial and final solute concentration

equilibrium solute concentration in solution and hence, computation of the mass adsorbed by the adsorbent, over the experimental range of initial solute concentrations (Equation 6.1).

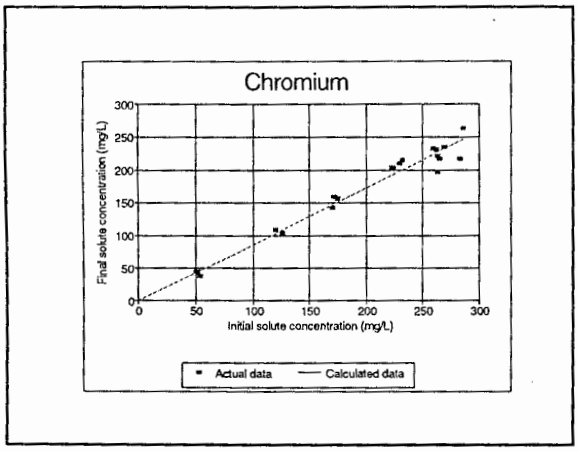

Figure 6.5
Chromium: relationship between initial and final solute concentration

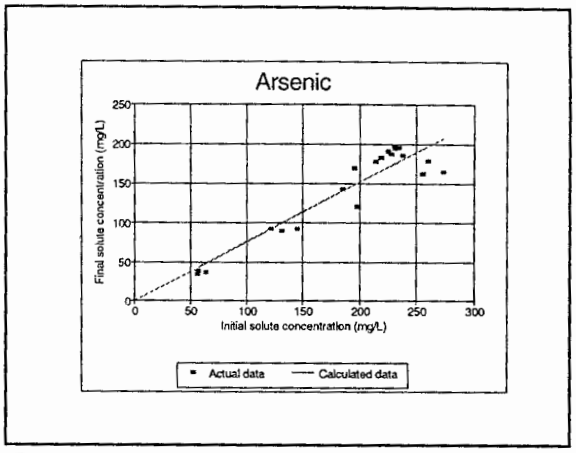

Figure 6.6
Arsenic: relationship between initial and final solute concentration

Table 6.3 Details of regression analysis: relationship between initial and final solute concentrations

Metal	R squared	X coefficient	No. of observations
Copper	0.807	0.140	21
Chromium	0.967	0.862	21
Arsenic	0.884	0.758	21

It is also of importance to examine the values of the X coefficient generated. The relationship can be expressed as shown below:

$$CAe = X.\ CAo \qquad 6.1$$

where,

CAe = Solute concentration at equilibrium
CAo = Initial solute concentration
X = X coefficient or gradient of the linearised data

In this case, the smaller the numerical value for the X coefficient, the greater the degree of affinity of the municipal solid waste to the metal in question. The degree of affinity is therefore; copper (0.140) > arsenic (0.758) > chromium (0.862).

By nature of a comparison, the Freundlich equilibrium distribution coefficient (K_F) may be considered as a measure of affinity between solute and adsorbent (Murali *et al,* 1983). The degree of affinity of the metals with municipal solid waste is copper > arsenic > chromium; a factor of 10 differentiating between the three metals, at pH5.5. At pH6.4, arsenic >> chromium. At pH7.0, copper ≈ arsenic >> chromium. There would appear to be good agreement between the degree of affinity reported by the Freundlich isotherm and the values quoted above. The discrepancy at pH7.0 is probably a result of the poor variance value (0.76) obtained for the Freundlich isotherm for arsenic.

Also evident from Table 6.3 is the *apparent* absence of the influence of pH on equilibrium solute concentrations, in the pH range measured. It is important to note the experimental pH range was narrow, being only 5.5 to 7.0, and the experimental technique adopted in this investigation was not entirely satisfactory to observe this phenomena. Often, initial concentration of the adsorbing ions was not similar in each experiment trial, also three metals were simultaneously adsorbing from solution.

If a soil is reacted with a series of aqueous solutions with the same initial metal cation concentration but the aqueous solutions having an increasing value of pH, the degree of cationic adsorption will usually increase with increasing pH. A limitation can however be introduced, that of competing ligands in the soil solution. In the absence of competing ligands, a plot of metal cation adsorbed versus pH has a characteristic sigmoid shape known as an "adsorption edge" (Sposito, 1989). Anion adsorption onto soils is characterised by a plot termed an "adsorption envelope", and is a result of changes in the net proton charge on the soil particles, if the adsorptive anion does not protonate significantly. The decrease in hydrogen ion concentration with increasing pH produces a repulsion of the adsorptive anion from the soil particle. Therefore at low pH values, adsorption is high, rising to a maximum, then subsequently decreasing with increasing solution pH (Sposito, 1989).

To observe this adsorption phenomena directly from the analytical results was not possible (the results of the equilibrium studies are shown in Appendix B, Tables B-1, B-2 and B-3). The analytical results are difficult to evaluate, as the initial concentrations differ significantly for all of the metals, over the pH range. In the case of copper, solubility constraints were experienced. The initial concentration of copper in solution was the major influence on the mass of solute adsorped, and in the case of copper this value was determined by the pH. At pH5.5 copper in solution approximated $60mg\ell^{-1}$, while at pH7.0, copper in solution approximated $27mg\ell^{-1}$. In two instances in the kinetic trials, the maximum copper in solution at pH6.4 was lower than that at pH7.0. The probable cause of this oddity was the too rapid addition of sodium hydroxide whilst adjusting the pH, causing excess precipitation of copper, an effect of localised high pH. There is another form of representation of the effect of pH on adsorption, that is to evaluate the percentage adsorption with change in pH. This is a less sensitive method of data analysis, but can be used to examine trends. This is shown in Table 6.4. For all the metals under consideration, the highest percentage adsorption was achieved at pH5.5, while the percentage adsorption at pH6.4 and pH7.0 was very similar.

Table 6.4 Variation of adsorption with pH

Metal	pH	Percent adsorption	Metal	pH	Percent adsorption
Copper	5.5	86.9	Chromium	5.5	21.1
	6.4	78.9		6.4	10.3
	7.0	79.1		7.0	10.4
Arsenic	5.5	34.3			
	6.4	20.6			
	7.0	23.2			

6.4 KINETICS OF ADSORPTION

The kinetics of the adsorption of copper, chromium and arsenic onto municipal solid waste were successfully described by the modified Freundlich equation shown below.

$$q - = K_a C_o t^{1/m} \qquad 3.10$$

where,

Co = initial solute concentration
t = time
K_a = constant
m = constant

The modified Freundlich equation is generally regarded as empirical (Aharoni *et al*, 1991b). However, the commonly used kinetic techniques are based on the assumption that the reactions are either unidirectional or discrete (Harter, 1991). The reaction under consideration involves three metals, themselves relatively complex in nature, reacting with a heterogeneous solid, municipal solid waste. It would seem probable that even if the reaction conformed to one of the simple kinetic orders of reaction it would only be fortuitous rather than an indication of the reaction mechanism. Chemical interactions between the solute and adsorbent may comprise of (Sparks,1989):

(i) formation or rupture of a bond between sorbate and surface;
(ii) further reaction between adsorbed species; and,
(iii) rearrangements of the solid structure and formation or disappearance of solid species.

Sparks (1989) states that (with soils) it is often incorrect to apply simple kinetic models such as first- or second-order to activated adsorption, as reacting solid surfaces are rarely

homogeneous, and because the effects of transport phenomena and chemical reaction are often experimentally inseparable. There would appear no reason why this statement should not equally apply to heterogeneous solids such as municipal solid waste.

The use of mechanistic rate laws to study adsorption phenomena assumes that only chemical kinetics are being studied, any physical aspects are ignored (Skopp, 1986). Most soil reactions of interest to soil scientists are heterogeneous solid-liquid reactions. These reactions usually take place by means of a multi-step mechanism that include mass transfer limitations, as well as chemical reactions (Aharoni *et al*, 1991a). The application of the simple kinetic relationships to complex systems is fraught with problems and caution should be exercised. Sposito discusses transport controlled adsorption kinetics in Chemical equilibria and kinetics in soils (1994) and states that *any surface reaction that involves chemical species in aqueous solution must involve a precursory step in which these species move toward a reactive site in the interfacial region.* He notes that *if the time scale for the transport step is comparable or much longer than that of the chemical reaction, the kinetics of adsorption will reflect transport control, not reaction control.*

Expressions such as the modified Freundlich equation are often successful when applied to various processes involving solid-fluid reactions, although initially developed by researchers investigating solute adsorption on soils. The characteristics of a reaction conforming to the modified Freundlich equation are rapid initial adsorption, the sorption rate decreasing with time. A generalised diagram is shown below.

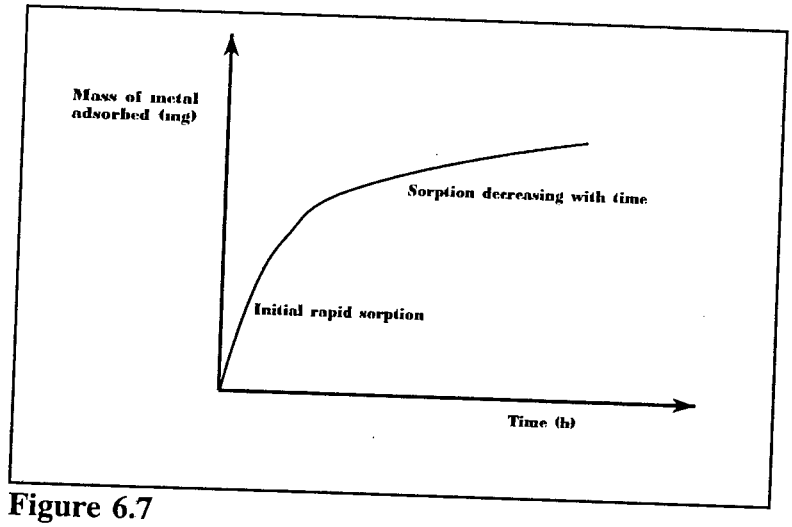

Figure 6.7
Characteristic curve of the modified Freundlich equation

6.4.1 Kinetic rate constants

The kinetic constants (K_a) for copper and chromium are consistent at the various pH values. The rate constants for arsenic show a greater variability. The results for copper and chromium were analysed in duplicate and any discrepancies in results were re-analysed. This ensured accurate reporting of these analytical results. This option was not available when

analysing arsenic and probably accounts for the greater variability of the results. Rate constants for copper were the highest, arsenic intermediate, with chromium being the lowest. The relevant results are tabulated below in Table 6.5. Also tabulated is a parameter often reported by researchers; the half reaction time ($0.5t_{total}$). The half reaction time is indicative of the speed of the chemical reaction. It is defined as the time taken for 50 percent of the total reaction to occur. Copper is very strongly adsorbed, as can be seen by the extremely short times calculated for the half reaction time ($0.5t_{total}$). The half reaction times are longer for chromium and arsenic but still average only 1 hour. This method of data analysis is not sensitive. It does, however, provide an indication of the relative speeds of the adsorptive reaction.

A complete summary of the results from the kinetic trials is shown below in Table 6.5 as constant reference is made to these results during this chapter.

Table 6.5 Summary of results from kinetic trials

Coding	pH	Initial concn. [C_o] ($mg\ell^{-1}$)	Final concn. [Ce] ($mg\ell^{-1}$)	Mass sorbed (mg)	Sorption rate coefficient [K_a] (h^{-1})	Constant [1/m]	SE	Half reaction time [$0.5t_{total}$] (h)
Copper A	5.5	63.6	8.8	55.6	0.722	0.055	2.93	0.0001
Copper B	5.5	53.2	8.4	44.8	0.677	0.063	3.95	0.0000
Copper C	5.5	65.1	11.9	53.2	0.668	0.068	2.37	0.0000
Copper D	6.4	9.6	1.3	8.3	0.629	0.096	0.92	0.0223
Copper E	6.4	14.4	2.5	11.9	0.817	0.061	1.40	0.0000
Copper F	6.4	21.3	0.3	20.7	0.766	0.081	1.00	0.0039
Copper H	7.0	22.1	2.4	19.7	0.738	0.059	1.02	0.0002
Copper I	7.0	27.4	5.0	22.4	0.825	0.064	2.74	0.0000
Chromium A	5.5	263	221	42	0.080	0.182	5.93	0.8
Chromium B	5.5	265	217	48	0.076	0.237	4.98	1.8
Chromium C	5.5	263	196	67	0.096	0.243	7.18	1.8
Chromium D	6.4	269	234	35	0.057	0.252	5.55	1.9
Chromium E	6.4	262	230	32	0.065	0.152	3.07	0.5
Chromium F	6.4	259	232	27	0.051	0.189	2.03	0.9
Chromium G	7.0	223	203	20	0.062	0.099	2.59	0.04
Chromium H	7.0	224	202	22	0.050	0.174	1.99	0.9
Chromium I	7.0	230	209	21	0.057	0.162	2.58	0.4
Arsenic A	5.5	255	163	92	0.199	0.157	5.32	0.5
Arsenic C	5.5	260	179	76	0.107	0.347	8.84	4.3
Arsenic D	6.4	228	187	41	0.055	0.368	6.83	1.1
Arsenic E	6.4	225	191	34	0.024	0.567	10.3	0.4
Arsenic F	6.4	231	197	34	0.090	0.155	3.77	0.3
Arsenic G	7.0	238	186	52	0.167	0.089	6.48	0.01
Arsenic H	7.0	219	183	36	0.090	0.185	3.32	0.6
Arsenic I	7.0	214	178	36	0.070	0.286	6.38	0.6

6.5 RATE OF REACTION: ADDITIONAL CONSIDERATIONS

The modified Freundlich equation is often successful when applied to various processes involving solid-fluid reactions. In the case of soils, kinetic data obtained experimentally often do not conform to the rate laws, but often can be described by some simple semi-empirical equation, such as the modified Freundlich equation. At low values of time, the modified Freundlich equation is frequently germane, at intermediate values of time the Elovich equation is typically applicable, at high values of time the pseudo first-order equation being appropriate (Aharoni *et al*, 1991a).

Adsorption reactions on soils may be classed as slow or rapid. Slow reactions are those in which processes taking place at the solid phase are rate determining (section 3.3.2). These rate determining processes may include: surface diffusion; diffusion in micropores; penetration of the solute into micropores in the solid; diffusion into the bulk of the solid, etc. (Aharoni *et al*, 1991a).

Researchers in the soil science field have examined this phenomena (Aharoni *et al*, 1991b) and have found when processes taking place at the solid phase are rate determining, it is often observed that a plot of the reciprocal of the rate against time is S-shaped, and other semi-empirical equations may be applicable at different reaction times. The phenomena of the S-shaped curve is indicative that reactions at the solid phase are associated with activated diffusional processes, such as surface diffusion or bulk penetration, where chemical bonds are ruptured and formed along the diffusional path.

Analysis of the experimental results indicated the rate of the chemical reaction was determined by activated diffusion processes taking place on the solid phase. Further analysis of the data showed the data conformed to a generalised model indicative of heterogeneous adsorption. This is a process where a solute diffuses in solid media that has different properties (section 3.3.6).

Consider the modified Freundlich equation, where

$$q = kt^{v} \qquad 3.11$$

Then,

$$Z = (dq/dt)^{-1} = (1/vK)t^{1-v} \qquad 3.14$$

Plots of the reciprocal of the adsorption rate (Z) versus time(t) or q (amount sorbed) versus $\log_e t$, for various soil reactions and other solid-fluid processes are usually S-shaped: convex at small values of time, concave at large values of time, and linear at some intermediate range of time. The generalised expression, S-shaped Z(t) plots may be explained by models based on diffusion. Equations for diffusion in a heterogeneous medium lead to S-shaped Z(t) and q (amount sorbed) versus $\log_e t$ plots in which the intermediate linear part is dominant.

Consider the rate of adsorption of copper onto municipal solid waste at pH7.0, the coding being "copper H" (Figure 6.2). The adsorption of copper is initially extremely rapid. The

rate of reaction slows rapidly as the reaction progresses indicative in this case of diffusion control. Unfortunately measurements ceased after 32 hours therefore the latter part of the S-curve (convex at large values of time) is unavailable. Aharoni (1991b) reports the modified Freundlich is linear for times less than 50 hours when data is plotted as amount sorbed (q) versus the square root of time ($\sqrt{t}$), after the initial inflexion at low values of time. The linear relationship between the square root of time and mass of solute adsorped is a characteristic of intraparticle diffusion.

Consider the rate of adsorption of chromium onto municipal solid waste at pH6.4, the coding being "chromium D". The adsorption of chromium is rapid, diffusional control is evident by the beginning of the S-shaped curve. Again measurements ceased after 32 hours. Consider the rate of adsorption of arsenic onto municipal solid waste at pH7.0, the coding being "arsenic F". The adsorption of arsenic is rapid, diffusional control is evident by the beginning of the S-shaped curve. As mentioned, equations for diffusion in a heterogeneous medium lead to S-shaped Z(t) and q (amount sorbed) versus $\log_e t$ plots in which the intermediate linear part is dominant. It can be seen the linear part of the curve is dominant in all cases, though more pronounced with chromium and arsenic (Figures 6.11 and 6.13, respectively).

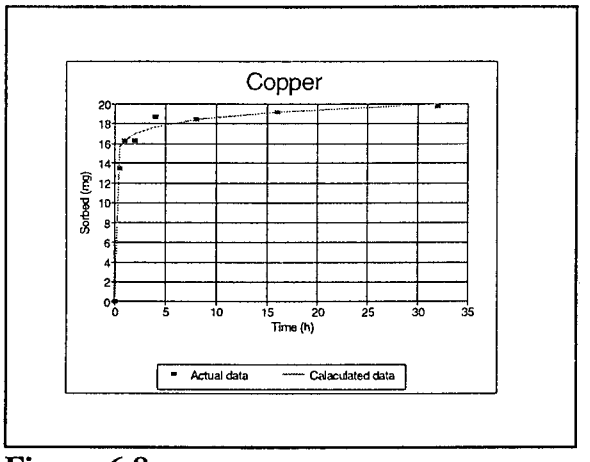

Figure 6.8
Adsorption of copper at pH 7.0 (copper "H")

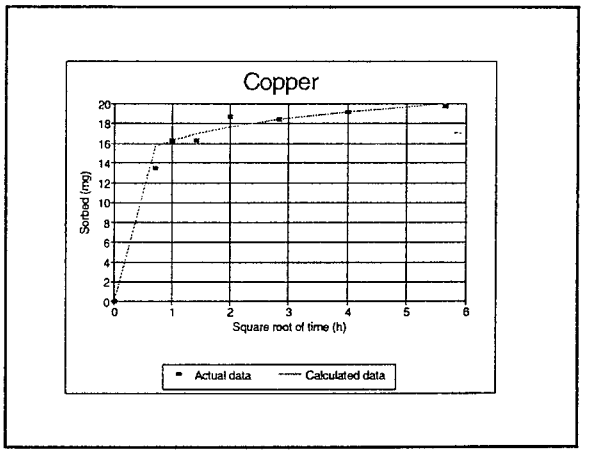

Figure 6.9
Mass of copper adsorbed (mg) versus square root of time (h)

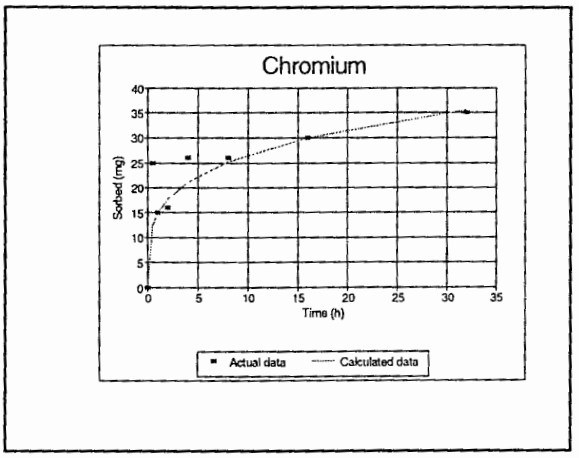

Figure 6.10
Adsorption of chromium at pH 6.4 (chromium "D")

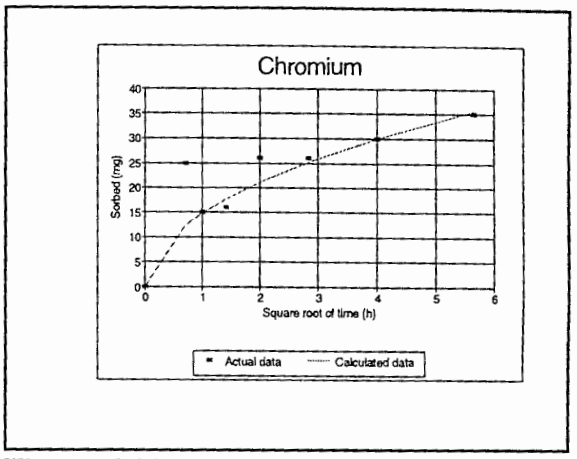

Figure 6.11
Mass of chromium adsorbed (mg) versus the square root of time (h)

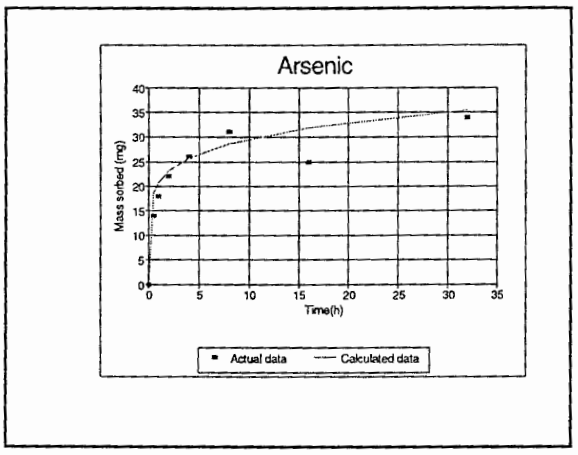

Figure 6.12
Adsorption of arsenic at pH 7.0 (arsenic "F")

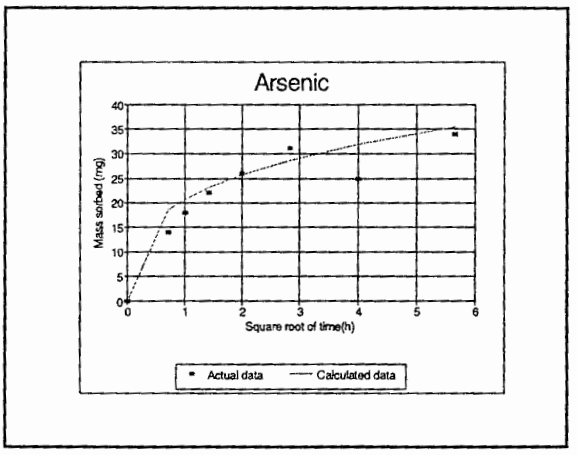

Figure 6.13
Mass of arsenic adsorbed (mg) versus the square root of time (h)

The results of this method of data analysis conformed to a generalised model indicative of heterogeneous adsorption. This confirms the results from the equilibrium studies, where the results obtained were successfully described by the Freundlich isotherm. Adherence to the Freundlich isotherm is generally considered to indicate adsorption onto a heterogeneous surface.

6.6 SORPTION RATE

The kinetic experiments were carried out at three pH levels; 5.5, 6.4 and 7.0. These pH values were adopted as they virtually cover the range which can occur in the full size landfill. It is important therefore, to examine the effect of pH on adsorption rate. The quantity of

adsorption that occurs at these pH values has been examined in section 6.3. The three modelled fits are shown overleaf for each metal at the relevant pH values.

Adsorption of copper at all three pH values is characterised by a curve that rises sharply to a plateau (Figures 6.14, 6.15 and 6.16). The initial concentration of the solution plays a larger role than one would anticipate, accelerating adsorption rate. This can be immediately observed in Figure 6.14 where copper A and C are identical and copper B is displaced as the initial concentration was lower by $10mg\ell^{-1}$ (see Table 6.5). The characteristic curve is similar at all pH levels investigated. Also, the effect of initial concentration is consistent at the different pH levels. For copper, agreement is good between the different experiments at the same pH.

The characteristic curve depicting the adsorption rate of chromium is more rounded than that of copper, adsorption continuing at a faster rate than that of copper, at higher values of time (Figures 6.17, 6.18 and 6.19). At pH5.5 (Figure 6.17) there is close agreement between chromium A and chromium B, whereas chromium C differs substantially. The lack of agreement is caused by the unusually large degree of adsorption of chromium C when compared with the two other experiments conducted at the same pH. All three trials commenced with the virtually the same initial concentration. On completion of the trial, adsorbent A adsorped 42mg, adsorbent B adsorped 48mg, while adsorbent C adsorped 67mg. This discrepancy can only be attributed to the adsorbent. At pH6.4 (Figure 6.18), the higher the initial chromium concentration, the greater the mass of chromium adsorbed. Chromium initial concentrations were 269mg (D); 262mg (E) and 259mg (F). Chromium adsorbed was 35mg (D); 32mg (E) and 27mg (F). At pH7.0 (Figure 6.16) agreement between experiments is good, with only a slight dispersion at larger values of time. There is only a difference of 2mg between the final equilibrium values.

Arsenic adsorption at pH5.5 (Figure 6.20) gives widely differing characteristic curves. The characteristic curve for the adsorption of arsenic (in general) is similar to that of chromium. Arsenic A is similar to the characteristic curve at other pH values, has a lower standard error (5.32 *versus* 8.84) and is probably more representative than Arsenic C. At pH6.4 (Figure 6.21), agreement is excellent between arsenic E and F with arsenic D again varying at larger values of time. The effect of initial concentration is not evident with arsenic D. Arsenic D has the lowest initial concentration of the three trials (187mg) and shows the largest degree of adsorption (41mg). In comparison, Arsenic E and F initial concentrations were 225mg and 231mg respectively, the mass of arsenic absorbed being 34mg in both cases. At pH7.0 (Figure 6.22) agreement is also good for arsenic adsorption, with the larger initial concentration in experiment G displacing the rate curve.

Another factor to consider is the half reaction time ($0.5t_{total}$) (calculated values are shown in Table 6.5). The half reaction time is indicative of the speed of the chemical reaction. It is defined as the time taken for 50 percent of the total reaction to occur. The half reaction time in this case is not a particularly sensitive method of analysis, but it can be seen that the half reaction times did not differ substantially throughout the range of pH values employed. The effect of pH on reaction rate was not significant. The half reaction time for the adsorption of copper is almost instantaneous. For both chromium and arsenic the adsorption rate was slower. It is of interest to examine the experimental trials with the lowest standard error in each pH range. For arsenic the lowest standard error occurs for trials A, F and H. The

average half reaction time for these three trials is 0.4h. For chromium the lowest standard error occurs for trials B, F and H; the average half reaction time for these trials is 1.2h.

In evaluating the information above, it is important not to underestimate the initial concentration of solute in solution when considering the rate of adsorption and the mass of solute adsorbed. This has a radical effect on rate of adsorption. It is also evident that the rate of copper adsorption far outstrips both chromium and arsenic. The rate of adsorption may be categorised in the following order:

copper >> arsenic > chromium

With an heterogeneous adsorbent such as municipal solid waste there is a surprising degree of similarity in the results from the kinetic trials, especially when considering only 50g of solid waste was employed in each separate experiment. It is probable that, if larger sub-samples were employed in the experimental procedure, variances between individual experiments conducted at the same pH value could be minimised.

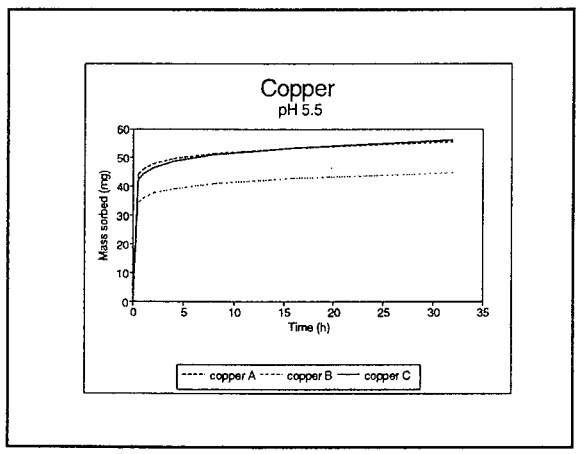

Figure 6.14
Copper: model fit at pH 5.5

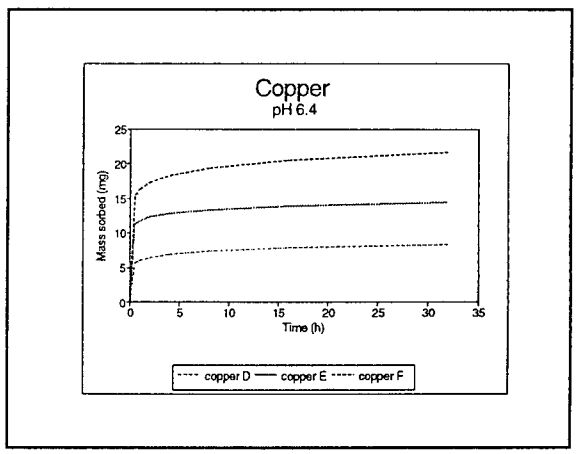

Figure 6.15
Copper: model fit at pH 6.4

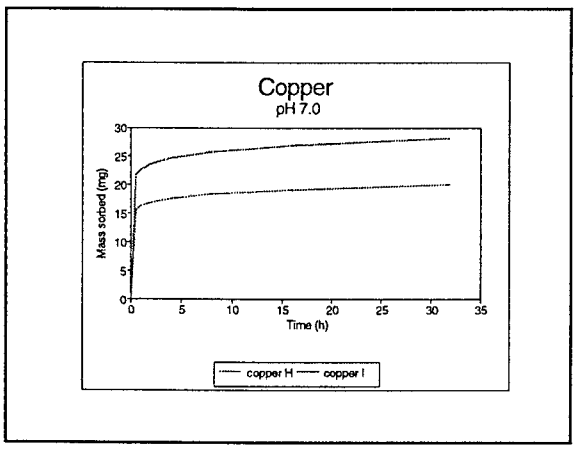

Figure 6.16
Copper: model fit at pH 7.0

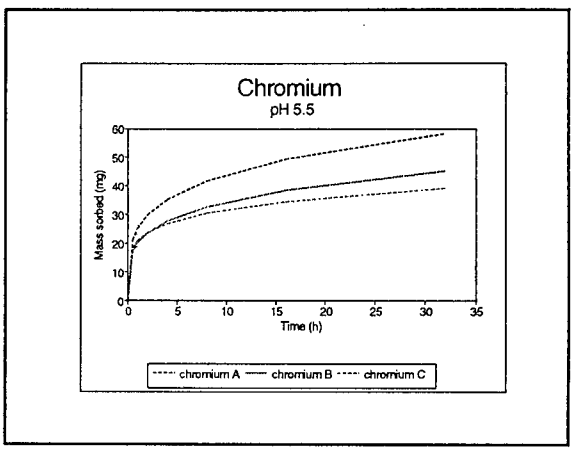

Figure 6.17
Chromium: model fit pH 5.5

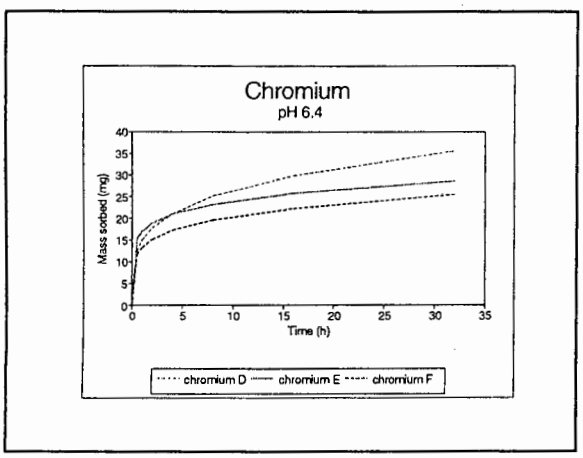

Figure 6.18
Chromium: model fit at pH 6.4

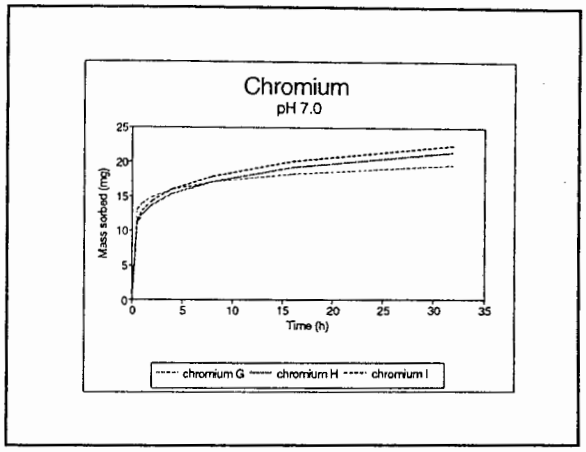

Figure 6.19
Chromium: model fit at pH 7.0

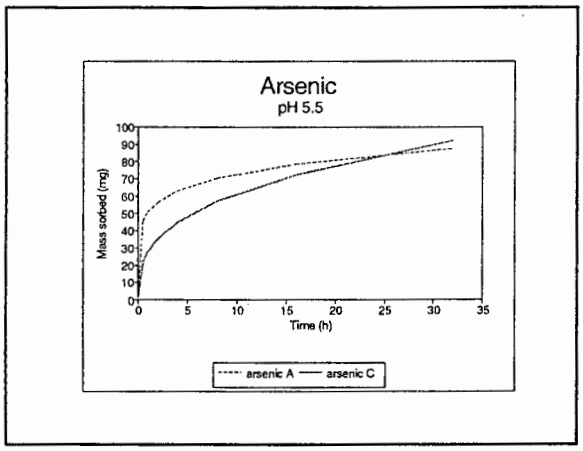

Figure 6.20
Arsenic: model fit at pH 5.5

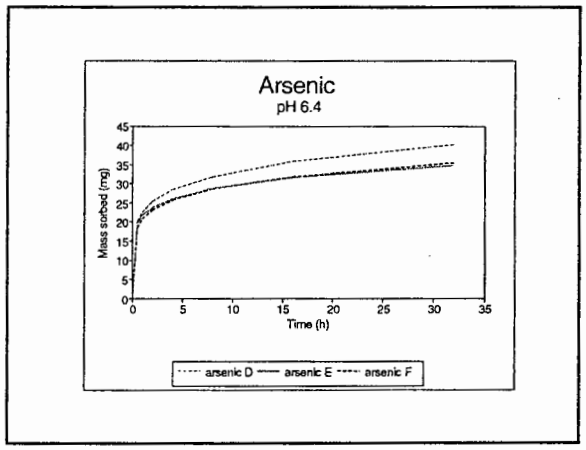

Figure 6.21
Arsenic: model fit at pH 6.4

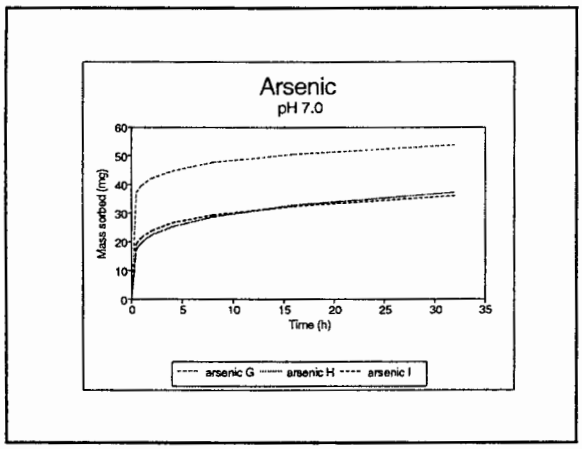

Figure 6.22
Arsenic: model fit at pH 7.0

6.7 SORPTION MECHANISM

The following items have been discussed; speciation of metals present, and their physical characteristics; the compliance of the metallic ions to the Freundlich isotherm, and the affinity of the various metallic ions to the adsorbent; the significance of the suitability of the modified Freundlich equation in describing the kinetics of adsorption and the rate of sorption of copper, chromium and arsenic. Information from the preceding sections will now be reviewed with the objective of characterising the solute adsorption mechanism. However, at the outset it should be noted that formulating reaction mechanisms for heterogeneous adsorbents can be tenuous (Harter, 1991). In principle, the requirements to investigate an adsorption mechanism include accurate adsorption data on well defined surfaces from well defined solutions at various temperatures, coupled with reliable thermodynamic data (Parfitt *et al*, 1983). All of the aforementioned are lacking.

In section 6.2 the speciation and size of the metallic ions was scrutinised. Copper is present in the form of a divalent cation. In aqueous solution, in the pH range under consideration, the hydrated ion is present as $Cu(H_2O)_6^{2+}$ and has a distorted octahedral structure. Chromium is present in the hexavalent form. The chromate ion (CrO_4^{2-}) predominates at pH values greater than 6.45. The chromate ion has a tetrahedral structure with four oxygen atoms bound to a central chromium atom. Arsenic is present in the pentavalent form. $H_2AsO_4^-$ (mono-ortho-arsenate ion) is the predominant species for pH values from 3.6 to 7.3. Mono-ortho-arsenate ion has a distorted tetrahedron structure.

In section 6.3 adsorption isotherms were discussed. Two important factors were revealed. Adherence to the Freundlich isotherm is generally considered to indicate adsorption onto a heterogeneous surface. Values obtained for the Freundlich equilibrium distribution coefficient (K_F) may be considered as a measure of affinity between solute and adsorbent. Over the pH range of the laboratory studies, the degree of affinity of the metals with municipal solid waste was copper > arsenic > chromium; this was confirmed by additional graphical analysis.

In section 6.5 the modified Freundlich equation was examined to determine reasons for its success in describing solid-fluid reactions. Researchers in the field of soil science have found the use of the modified Freundlich equation is indicative that reactions at the solid phase are associated with activated diffusional processes. Additional examination showed the data conformed to a generalised model indicative of heterogeneous adsorption. This examination confirmed observations from equilibrium studies, where adherence to the Freundlich isotherm is generally considered to indicate adsorption onto a heterogeneous surface.

In section 6.6 the rate of sorption was studied. It was found that the rate of copper adsorption was extremely rapid, the rate of adsorption of arsenic being intermediate, with chromium adsorption being the slowest of the three metals. The initial concentration of the metal in solution was of importance when examining both the mass of solute adsorbed and the rate of sorption.

The adsorption of small ions is strongly but not exclusively determined by electrical interactions (Lyklema, 1983). However, the relative size of the ions in solutions was investigated. As a first approximation, the presence of the hydrogen ions was neglected, if

more stringent calculations were required (i.e. if the relative size of the ions were close), they would be performed. Additionally, there are undoubtedly hydrogen ions clustered around both the chromate ion and the arsenate ion as in the case of copper ion, in an aqueous solvent. It can be seen below in Table 6.6, the copper ion is far larger than both the chromate and arsenate ions which are of a similar size. Copper is adsorbed far more rapidly than either chromium or arsenic, indicative that the adsorption in this case is determined by electrical interactions, and not the size of the relevant ions. Copper is present in the form of a cation while both chromium and arsenic are in the form of an anion.

Table 6.6 Comparison of physical data of the relevant ions

Ion	Formula	Ionic radii (Å)	Bond length (Å)	relative size to the chromate ion
Copper	$Cu(O)_6^{2+}$ (H ions neglected)	0.87	1.94 (x) 2.40 (y).	2.5
Chromium	CrO_4^{2-}	0.63	1.63.	1.0
Arsenic	AsO_4^{3-}	0.70	1.67	1.1

Unfortunately, a good fit of adsorption data to the less complex linear isotherms, such as the Langmuir or Freundlich isotherm does not in itself constitute any proof of any specific adsorption mechanism. Attempts were made to fit the equilibrium results to the system of isotherm classification, developed by Giles and co-workers (1974a; 1974b); the S, L, H and C isotherms. These isotherms can by used to assist in interpretation of adsorption mechanisms, and much useful information can be obtained. There were insufficient data points to for these isotherms to be properly constructed. However, the significance of the Freundlich isotherm to characterise adsorption onto a heterogeneous surface was reinforced by the applicability of the modified Freundlich equation in section 6.5, where equations for diffusion in a heterogeneous medium lead to S-shaped Z(t) and q (amount sorbed) versus $\log_e t$ plots in which the intermediate linear part is dominant. Also the applicability of the Freundlich power coefficient to determining the affinity of the various solutes to the adsorbent was confirmed by the additional graphical constructions in section 6.3.

In the determination of an adsorption mechanism there are a number of facts to consider, two of which are readily apparent. In aqueous solutions, adsorbents are usually charged as there is always ionic species present and typically there is preferential absorption/desorption of those species. At any solid/aqueous interface adsorption of these ions is the rule rather than the exception. Both the solution and the adsorbent must maintain electronic neutrality. If a cation is adsorped there is either the co-adsorption of an anion or the desorption of a corresponding cation (Lyklema, 1983). As shown in Table 4.5, there was a change in pH in the course of the experimental procedure during the kinetic trials. The experiments conducted at initial solution pH5.5 furnished a final solution pH of 7.0; the experiments conducted at initial solution pH6.4 provided a final solution pH of 8.0 and the experiments

conducted at pH7.0 showed a final pH varying from 8.1 to 8.6. There is an obvious increase in hydroxyl ions during the course of the experiment. This would appear to indicate an exchange of the anions, chromium and arsenic for hydroxyl groups. Lindsay suggested (cited by de Haan *et al*, 1976) that all copper reactions in soil could be summarised by the general equation

$$Cu^{2+} + \text{soil} \rightleftharpoons \text{Cu-soil} + 2H^{+}$$

This reaction with the municipal waste would maintain electroneutrality, the corresponding anion exchange between chromium and arsenic for hydroxyl ions would also maintain electroneutrality. Additionally, this postulated reaction mechanism is confirmed by the pH measurements, and the indications that the surface is heterogeneous, allowing hydrogen ions and hydroxyl ions to be present at the solid interface. There is far less copper in solution than either chromium or arsenic. Therefore the pH would rise during the course of the experiment as less hydrogen ions would be exchanged than hydroxyl ions. This analysis would be complimentary to the influence of diffusion. The diffusional influence is caused by the ions diffusing past each other in an effort to get to the surface of the adsorbent, not diffusion of ions into the inner recesses of the solid phase, as would be commonly encountered.

Adsorption of three metallic ions onto a heterogeneous substance such as municipal solid waste is a complex system. To definitively examine the adsorption mechanism is extremely difficult, especially considering the adsorptive medium in conjunction with the metallic ions. However, in the absence of further experimental data the above conclusions appear reasonable.

6.8 TRACER STUDIES

Initial laboratory work (section 4.7.3(a)) indicated the suitability of lithium sulphate as a tracer in an environment where municipal solid waste is predominant. The percentage of lithium adsorbed was less than 2 percent (Table 4.11). This was confirmed in the pilot scale studies were the recovery of lithium bettered 92 percent. Of the 1027mg of lithium added, 954mg was recovered. The pilot-scale tracer studies ceased after 317 days, at that point lithium was still evident, albeit in a very low concentration. It is probable, that if monitoring had continued, the recovery of lithium would have been greater.

The characteristic curve of the tracer conformed to that expected. A high degree of non-ideality was exhibited, the variance was calculated at 3338, while the mean residence time was 113 days. Maximum lithium recovery occurred after 84 days, the lithium concentration of the leachate at that time was 2.003mgℓ^{-1}. The only departure from that expected on a full scale landfill is probably the initial rapid rise of lithium in the leachate, probably caused by a combination of preferential channelling and wall effects from the column. The characteristic curve, although not ideal, is not unlike commonly occurring **E** curves obtained from industrial equipment where the peak of the curve does not necessarily occur at the mean

time and "tailing" does often occur (Denbigh *et al*, 1971). The rapid initial rise commented on earlier, is not a common phenomena.

6.9 CO-DISPOSAL AT PILOT-SCALE

As reported in section 4.7.4, a concentrated solution of copper, chromium and arsenic was co-disposed with the municipal solid wastes in columns 3 and 5. Analytical results are reported in Appendix E. Tables E-1 and E-3 tabulate leachate volumes and metal concentrations for columns 3 and 5 respectively; Tables E-2 and E-4 tabulate the associated chemical data (pH, COD, etc.,) for columns 3 and 5. The mass of metals introduced into both columns 3 and 5 was copper, 88.4g; chromium, 256.1g and arsenic, 256.7g. The time duration of the experiment with column 3 was 235 days, the average volumetric displacement of leachate was 19.2ℓweek^{-1}. The time duration of the experiment with column 5 was slightly shorter, 221 days. The average displacement of leachate was 18.5ℓweek^{-1} .

6.9.1 Copper

Results from the monitoring of copper concentration of leachate from columns 3 and 5 are shown graphically in Figure 5.29. The initial concentration of copper in the leachate from column 3 was 0.05mgℓ^{-1}, the highest copper concentration was recorded was 0.11mgℓ^{-1}. Over the entire period of monitoring (235 days), the concentration of copper in the leachate from column 3 averaged 0.05mgℓ^{-1}, The initial concentration of copper in the leachate from column 5 was 0.07mgℓ^{-1} this was not exceeded for the entire duration of the experiment. The final copper concentration after 221 days was 0.04mgℓ^{-1}.

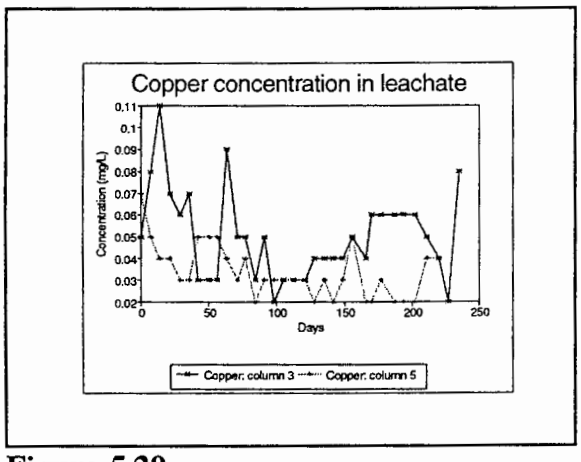

Figure 5.29
Copper concentration in leachate from columns 3 and 5

As stated in Section 5.4.5 although 88.4g of copper are added, virtually all of this copper would precipitate upon introduction into the column, a consequence of solubility effects. There was not any doubt concerning of the lack of mobility of copper in the landfill environment, even an acetogenic landfill were pH levels approximate 5.5, at the outset of this investigation. The mobility of copper in various soils was reported in section 2.8.1.3(d) All the researchers reviewed (Korte *et al*, 1976; Aringhieri *et al*, 1985; Sapek cited by Aringhieri *et al*, 1985) commented on the low mobility of copper, even at low pH levels. Korte and co-workers (1976) examined the mobility of copper with an initial solution of landfill leachate at a pH of 3. Copper was immobile in all the soils except a sandy Wigram, even then, its mobility was low. The kinetic trials only served to confirm this, the rapid adsorption of copper has already been discussed in this chapter. Additionally, only 4 percent of the copper adsorbed was desorbed in the desorption trials. It is probable that desorbed

copper would be re-adsorbed, as the liquid flows through the column contacting the remaining copper ions with adsorbent. The analytical results of the leachate from the pilot-scale columns confirms the work of previous researchers.

6.9.2 Chromium

Results from the monitoring of chromium concentration of leachate from columns 3 and 5 are shown graphically in Figure 5.30. Initially, chromium in the leachate from column 3 was not detectable. The chromium content of the leachate rose steadily to a maximum of $0.04mg\ell^{-1}$, this value was not exceeded for the duration of the experiment, the final chromium concentration was $0.03mg\ell^{-1}$ on Day 235. The average chromium content in the leachate from column 3 over the entire duration of monitoring was $0.03mg\ell^{-1}$. The initial chromium content of leachate from column 5 was $0.06mg\ell^{-1}$, The final chromium concentration was $0.02mg\ell^{-1}$ on Day 221. The average chromium content in the leachate from column 5 over the entire duration of monitoring was $0.04mg\ell^{-1}$.

The predicted chromium concentration in the leachate from column 3 is shown in Figure 5.54. Until Day 160 the model realises actual measurements well, with very little deviation. From Day 160 the model begins to overpredict actual conditions. Results from monitoring continue in the region of $0.03mg\ell^{-1}$ whereas the model begins to predict chromium concentrations in excess of $2mg\ell^{-1}$ in that time frame, with predicted chromium concentration rising to a maximum of $4.4mg\ell^{-1}$ on Day 390.

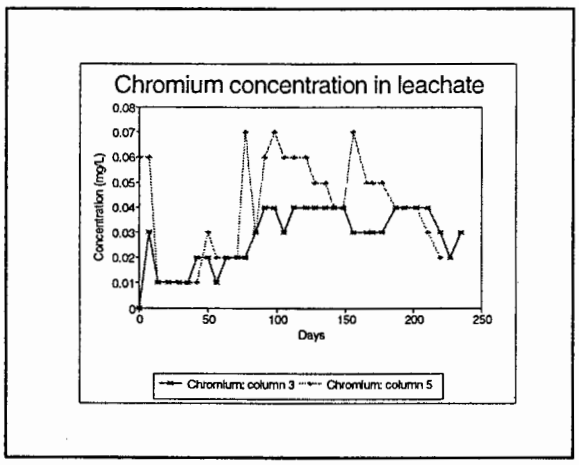

Figure 5.30
Chromium concentration in leachate from columns 3 and 5

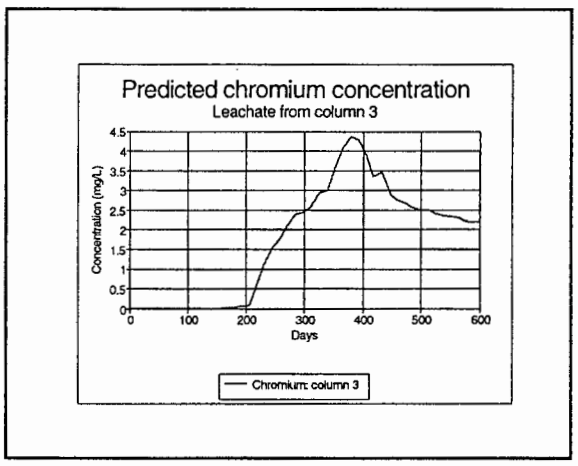

Figure 5.54
Predicted concentration of chromium in leachate from column 3

Some experimental considerations and the effect of the computational method were discussed briefly in section 5.4.5(c) and will not be repeated here. Although monitoring ceased on Day 235 and the calculations indicated a total residence time of 600 days this is not regarded as detrimental to a comparison of these results. It is extremely unlikely there would be any increase in actual chromium concentration in the column effluent. The computations assume

the only attenuation mechanism to be adsorption. There are other possible attenuation mechanisms (such as precipitation) available to inhibit chromium mobility. Again, at the outset of the experimental work indications from the literature review indicated that chromium to be immobile in the landfill environment. A brief review of the work of other researchers confirms this.

Researchers in the field of soil science consistently reported a low mobility of chromium(VI) in soils (section 2.9.1.3(d)). Sheppard *et al* (1992) investigated the desorption of chromium from both a sandy and clay soil. The authors reported that if soil remediation was required, it would be less expensive to remove the soil that attempt any chemical treatment as the chromium was so firmly fixated. McGrath *et al* (1990) reported on a trial that had taken place over 19 years, where soils had received a sewage sludge containing chromium; there had been no significant movement of the chromium during that time period. Other researchers (Calder, 1988; Bartlett *et al*, 1976) reported the reduction of chromium(VI) to essentially immobile chromium(III) in the presence of organic matter, under anaerobic conditions, regardless of pH.

The composition of leachate from the columns (Appendix E), the low percentage volatile solids of the municipal solid wastes (section 4.3.3), plus the very low volume of biogas generated (section 4.7.2(c)) confirmed the municipal solid waste to be fully stabilised. The configuration of the columns, the length of time the columns have been at field capacity, the large volume of water present in the columns, are all factors that indicate that viable areas of anaerobic conditions would likely exist in the columns. The kinetic studies were completed in an aerobic environment. In that environment the behaviour of the metals under consideration can be regarded as ideal.

Conventional theory dictates the pilot-scale landfill column should be considered as a packed column. Traditional columns employed in industry are composed of adsorbents such as activated carbon, silica gel or activated alumina. Adsorbents are generally available as irregular granules, extruded pellets and formed spheres. The size of adsorbents rarely exceed 6mm, the size reflecting the need to pack as much surface area as possible into a given volume (Coulson *et al*, 1991). The municipal solid waste was reduced in size prior to placement in the column, increasing the surface area. This reduction in size did not approximate the reduction in size of the solid waste employed in the laboratory scale trials (section 4.3.2). A major difference between the solid waste and conventional columns is that liquid can flow through certain components of the waste such as paper, cardboard etc. It is probable the area available for adsorption is increased greatly by this mechanism, increasing adsorption. This analogy is given credibility by the nature of the characteristic curve obtained from the tracer studies. The liquid initially flows rapidly through existing channels, longer exit times are provided by fluid passing through the particles of solid waste. Here also an additional variable is introduced. A requirement of industrial adsorbents is structural integrity. In an aqueous environment components of the solid waste will lose structural rigidity and will start to collapse, delaying elements of the liquid.

As mentioned in section 5.4.5(c), an additional factor worthy of consideration is the sample size utilised in the kinetic experiments. Only 50g was used, while the pilot-scale columns were packed with approximately 700kg of municipal solid waste. While sampling was exhaustive, solid waste is an extremely heterogeneous substance.

6.9.3 Arsenic

Results from the monitoring of arsenic concentration of leachate from columns 3 and 5 are shown graphically in Figure 5.31. The initial concentration of the arsenic in the leachate from column 3 was 17$\mu g\ell^{-1}$ rising in irregular steps to Day 194 when the concentration exceeded 2000 $\mu g\ell^{-1}$. Arsenic concentration in the leachate from column 3 remained at that level until the cessation of monitoring on day 235. Column 5 mirrored the behaviour of column 3, though at a reduced manner. The maximum arsenic concentration attained was 802$\mu g\ell^{-1}$ at Day 213; results were relatively constant from Day 188 at that level.

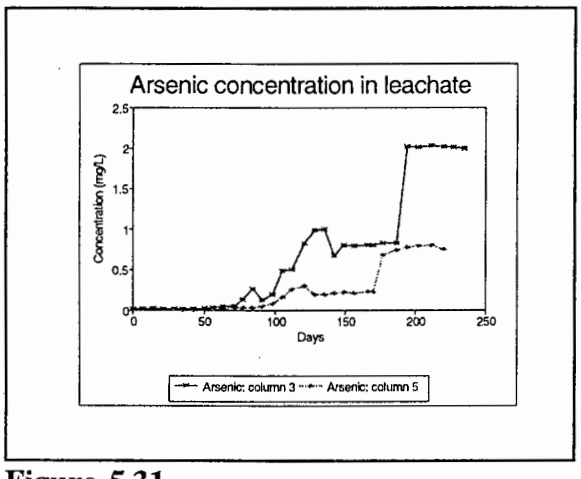

Figure 5.31
Arsenic concentration in leachate from columns 3 and 5

The predicted outcome of the co-disposal of arsenic was calculated in the same manner as that of chromium. Calculations predicted there would be an absence of arsenic in the leachate from column 3 during the total time period of 600 days. The results from desorption kinetic trials (section 5.4.3) showed that arsenic was the only metal of those under consideration that displayed any significant degree of desorption. This could not be allowed for in the calculation, and could account for the extremely low degree of error that is evident. There are not any significant solubility constraints with arsenic, whether it is in the form of arsenic(III) or arsenic(V), and if anaerobic conditions were experienced this would probably enhance the mobility of any arsenic present. In section 2.8.1.3(d) the behaviour of arsenic in soils under reducing conditions was reported. Reducing conditions convert arsenic(V) to arsenic(III). Arsenic(III) is 5 to 10 times more soluble than arsenic(V) increasing mobility.

In the case of arsenic it was unfortunate that the trials to did not proceed further, as reports of arsenic mobility are inconsistent (section 2.8.1.3(d)). However the degree of agreement between actual and predicted concentrations is excellent the maximum degree of error only being 2mgℓ^{-1} over the 235 day trial. Additionally, results appear to have stabilised at that level.

6.10 COMPUTATIONAL METHOD - GENERAL COMMENTS

The method employed to calculate the exit stream composition was reported in section 3.4.4 and section 5.4.6. The computation from the residence time data obtained from column 4 to provide suitable residence time data for column 3 and for the application of the pilot-scale studies to the full scale landfill proved to be successful. The calculated values for the mean, variance, total residence time and volumetric displacement of leachate are shown overleaf

in Table 6.7. The computational method retained the characteristic curve obtained in the lithium sulphate pulse experiment.

Table 6.7 Summary of actual and computed results: residence time distribution

	Volumetric displacement (ℓday^{-1})	Mean ($\bar{t}$)	Variance (σ^2)	Total residence time (days)
Tracer studies (Column 4)	5.21	113.2	3338	317
Co-disposal trials (Column 3)	2.75	214.3	11953	600
Application of pilot-scale studies to the full-scale landfill	3.73	153.4	6123	430

The computational method employed to calculate the exit stream metal concentrations employs a conventional chemical engineering mathematical approach the computational method is shown below in Figure 3.2

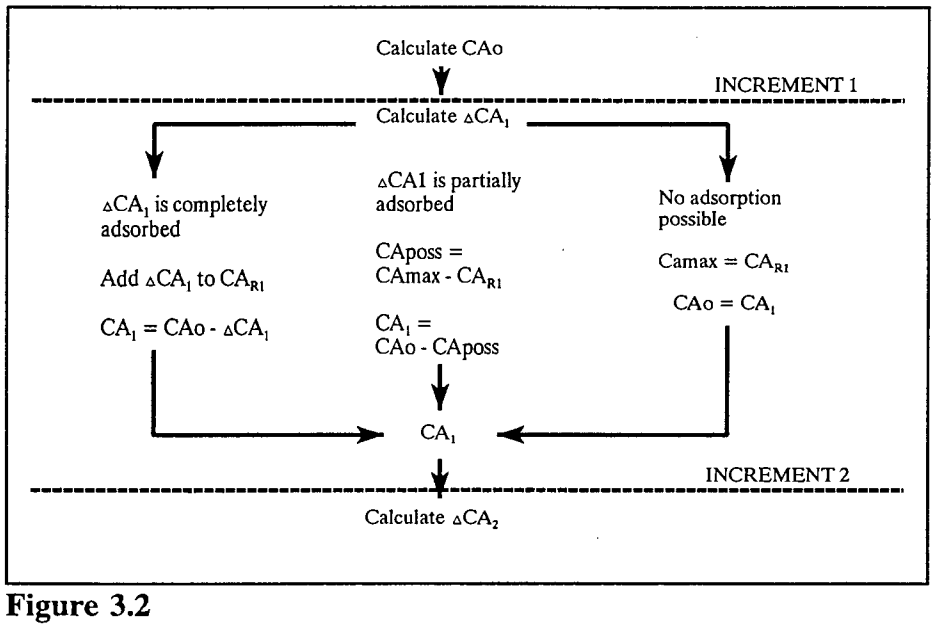

Figure 3.2
Illustration of computational method

Nomenclature

CAo	=	Solute concentration in fluid at t = 0 (gkg^{-1})
CA poss	=	Equilibrium solute concentration in adsorbent (gkg^{-1})
$\triangle CA_n$	=	Solute adsorbed in increment n (gkg^{-1})
CA_n	=	Solute concentration in fluid entering increment n (gkg^{-1})

The method is rigorous and accurate at low values of time. At larger time values the degree of accuracy is lowered. The incremental depth of the adsorbent is the problem area. The depth increment must be minimised for maximum accuracy, as the rate of adsorption is initially rapid and decreases with time. The depth increment must therefore be minimised to ensure the calculation accurately reflects the real situation within the column, where the residence time elements of fluid flow do not exceed the time required to reach equilibrium with the solid waste. The depth increment was minimised to 20mm. Using incremental depth of 20mm requires over 95 increments, as the column depth is 1940mm. This, together with the minimised time increment, requiring over 45 separate increments results in a spreadsheet in excess of 1.7Mb. At large values of time a smaller depth increment would ensure that each separate time increment of fluid would not spend excessive time in each increment of depth. Thus, at large values of time, it is possible the computed exit concentrations could be higher than that actually experienced.

6.11 APPLICATION OF THE PILOT-SCALE STUDIES TO THE FULL SCALE LANDFILL

As detailed in section 5.4.7 the application of the pilot-scale studies to the full scale landfill involved a worst-case study. The assumptions were:

(i) Precipitation occurring at Coastal Park Sanitary Landfill (from which the municipal solid waste was excavated) in the heaviest precipitation month falls on a continual basis;
(ii) no loss of moisture from the landfill, such as evapotransportation or run-off;
(iii) the landfill was at field capacity prior to co-disposal;
(iv) metal content in leachate from the landfill should not exceed the most stringent requirements prescribed by current South African legislation.

The assumptions are very stringent, and there is no doubt that the amounts of copper, chromium and arsenic determined to be suitable, would not cause any additional environmental damage to the area surrounding the landfill. The calculations revealed that when disposing of these metals in combination the mass of copper should not exceed $67gt^{-1}$; the mass of chromium in the form of chromium(VI) should not exceed $195gt^{-1}$; the mass of arsenic should not exceed $195gt^{-1}$. Rushbrook (1990) tabulated various maximum loading rates quoted in the United Kingdom by the various United Kingdom authorities. The values are shown in section 2.8.3, Table 2.16). The values for copper, chromium, and arsenic are

shown below in Table 6.7, together with the proposed values obtained in this study. When considering the co-disposal of heavy metals, the United Kingdom's Department of the Environment state that *limited evidence suggests an initial loading of 100g of soluble chromium, copper, lead or zinc per tonne of mature household waste is unlikely to produce a significant change in leachate concentration 3 metres distance from the heavy metal waste* (DOE, 1986). It should be noted that the DOE recommend, that if optimum attenuation is sought that co-disposal be practised with mature (that has been deposited between 1 and 5 years) municipal solid waste.

Table 6.7 Co-disposal loading rates

Constituent	Loading rate	Proposed loading rate
Chromium	$100gt^{-1}$*	$195gt^{-1}$
Copper	$100gt^{-1}$*	$67gt^{-1}$
Arsenic	$10gt^{-1}$* $10kgt^{-1}$* (for As in sulphide form)	$195gt^{-1}$

* adapted from Rushbrook, 1990

The calculated loading rates compare favourably with that quoted by the DOE. It must be noted:

(i) the loading rates quoted by the DOE are for a total heavy metal loading of $100gt^{-1}$ whereas the proposed loading rate totals $262gt^{-1}$ for chromium and copper in combination;

(ii) the DOE quote a depth of 3m while the proposed loading rates were calculated with a depth of 2m of municipal solid waste.

Discussion of the loading rate quoted for arsenic is more complex. The value quoted by Rushbrook is not repeated in the DOE literature such as Waste Management Paper No 20, Arsenic-bearing wastes (1980) or Waste Management Paper No 26, Landfilling wastes (1986). Both publications express concern that the concentration of arsenic in leachate does not exceed $10mg\ell^{-1}$. Cossu *et al* (1989) reviewed the co-disposal of industrial wastes, including the disposal of arsenic wastes. The researchers affirm the value quoted by Rushbrook, that of $10gt^{-1}$, and refer to test work completed by Blakey in 1984 (section 2.8.1.3(c)). It would appear that the leachate concentration is the controlling variable. If one does not exceed an arsenical concentration of $10gt^{-1}$ of municipal solid waste, the value of $10mg\ell^{-1}$ arsenic in leachate, will not be exceeded.

It is evident the loading rate values quoted by the DOE for arsenic are conservative. The DOE is concerned with additional factors such as the generation of arsine gas (section

2.8.3(c)). Arsine (AsH_3) is an extremely poisonous gas, with no effective antidote (DOE, 1980). Arsine is produced whenever a reaction generating nascent hydrogen occurs in the presence of arsenic. Hydrogen generation can occur under anaerobic conditions, especially acetogenic conditions (section 2.6.2).

In general, loading rates proposed from experimental work undertaken in this study concur with loading rates employed in the United Kingdom, recommended by the United Kingdom's Department of the Environment.

6.11.1 Full scale landfill operation - additional factors

The life of a landfill may be classified into three primary time frames (section 2.6.1): the acetogenic or acid producing phase; the methanogenic or methane producing phase; the stabilised or final maturation phase. The pilot-scale studies together with the kinetic experiments explored the adsorption of the relevant heavy metals onto stabilised municipal solid waste. A stabilised landfill is characterised by a leachate comprising of a; neutral pH; high level of alkalinity; low level of carboxylic acids; low degree of organic contamination or Chemical **O**xygen **D**emand (COD) and an extremely low production of biogas from the landfill. An acetogenic landfill is characterised by a leachate comprising of a; low pH; low level of alkalinity; high level of carboxylic acids; high degree of organic contamination with a virtual absence of biogas production from the landfill. A methanogenic landfill is categorised by leachate with a neutral pH; substantial generation of biogas with all other parameters being intermediate between the acetogenic and stabilised landfill.

Pohland (1986b) compiled data from a number of sources, indicative of the three primary stages of landfill life. This is shown overleaf in Table 6.8. Copper, chromium and arsenic are of primary interest. Other metals are also shown, for comparative purposes.

Table 6.8 Composition of landfill leachate and biogas from the difference phases of landfill age

(adapted from a review by Pohland *et al*, 1986b)

Constituent	Acetogenic landfill	Methanogenic landfill	Stabilised landfill
pH	4.7 - 7.7	6.3 - 8.8	7.1 - 8.8
Total Alkalinity ($mg\ell^{-1}$ as $CaCO_3$)	140 - 9650	760 - 5050	1460 - 4840
Total Volatile acids ($mg\ell^{-1}$ as CH_3COOH)	3000 - 18000	250 - 4000	Essentially absent
COD ($mg\ell^{-1}$ as O)	1500 - 71100	580 - 9760	31-900
Copper ($mg\ell^{-1}$)	0.005 - 2.2	0.03 - 0.18	0.02 - 0.56
Chromium ($mg\ell^{-1}$)	0.06 - 18	0.05	0.05
Lead ($mg\ell^{-1}$)	0.01 - 1.44	0.01 - 0.1	0.01 - 0.1
Nickel ($mg\ell^{-1}$)	0.03 - 79	0.01 - 1.0	0.07
Zinc ($mg\ell^{-1}$)	0.65 - 220	0.1 - 4.0	0.4
Cadmium ($mg\ell^{-1}$)	70 - 3900	76 - 490	76 - 254
Iron ($mg\ell^{-1}$)	90 - 2200	115 - 336	4 - 20
Methane (%)	< 1	30 - 60	0 - < 10
Carbon dioxide (%)	10 - 30	30 - 60	< 40
Nitrogen (%)	60 - 80	< 20	> 20
Oxygen (%)	0 - 5	0 - 5	> 5
Hydrogen (%)	0 - 2	< 0.1	Essentially absent

(a) Copper

It would be envisaged that copper would be relatively immobile in any age of landfill. The results collated by Pohland shown in Table 6.8 indicate copper to be mobile in an acetogenic landfill, less so in a methanogenic and a stabilised landfill. It is not unexpected that copper has a low degree of mobility in a methanogenic or a stabilised landfill. It is however surprising that it is mobile in an acetogenic landfill. Most researchers report the relative immobility of copper in organic soil, and report a tendency for copper to form stable organic complexes with organic matter in soil (section 2.8.1.3(d)). Also, soils having higher levels of organic matter are usually acidic in nature, as is the leachate from an acetogenic landfill.

Other researchers report the mobility of copper in soils to be low, and describe the adsorption of copper onto organic matter, clay minerals, and even pure quartz. Soil scientists have conducted trials examining the movement of various metals in soils over extended periods. Lundblad and co-workers (1949) added over 250kg of copper (per hectare) to an acid peat soil. After 5 years had elapsed only 0.2 percent of the copper added was removed from the top 5cm of soil (section 2.8.1.3(d)).

Results from this current study are presented below in Table 6.9. Copper is strongly adsorbed at all the pH levels shown, there is little evidence of significant desorption. (section 2.8.1.3(d)).

Table 6.9 Mass and percentage of copper adsorbed and desorbed at pH 5.5, 6.4 and 7.0

Metal and species	pH	Average mass sorbed (mg)	Percentage adsorption	Average mass desorbed (mg)	Percentage of metal adsorped that is desorbed
Copper(II)	5.5	50.9	86.9	-1.7	3.3
	6.4	14.1	78.9	0.5	3.5
	7.0	23.0	79.1	0.8	3.5

The mobility of copper is severely restrained in both a methanogenic and a stabilised landfill. The solubility of copper is very limited in an aqueous solution, in an anaerobic reducing environment even more so. The subject of sulphate reducing bacteria was addressed in section 2.8.2(a). Hydrogen sulphide is produced by sulphate reducing bacteria. Hydrogen sulphide is a strong reducing agent, it can react with copper causing precipitation of the copper as insoluble copper sulphide.

Table 6.8 reveals copper to be one of the least mobile metals tabulated. The work of other researchers, together with results obtained in this study (Table 6.9), are in agreement.

(b) Chromium

It would be anticipated that the mobility of chromium(VI) would be limited in any landfill of any age. The kinetic trials showed that although mass of chromium adsorbed was proportionally less than copper or arsenic, chromium was strongly bound, and showed little evidence of desorption (Table 6.10).

Examination of Table 6.8 shows that the chromium content of a leachate from an acetogenic landfill to be relatively high when compared with a methanogenic or stabilised landfill. Leachate from an acetogenic landfill contains high levels of soluble organic acids enhancing the mobility of chromium. The pH of the leachate is low, adsorption of chromium(VI) was

satisfactory in the kinetic trials at similar pH levels. The TCLP extraction fluid contains a carboxylic acid; acetic acid, which should approximate a leachate from an acetogenic landfill. The degree of approximation was not adequate in this instance.

Table 6.10 Mass and percentage of chromium adsorbed and desorbed at pH 5.5, 6.4 and 7.0

Metal and species	pH	Average mass sorbed (mg)	Percentage sorbed	Average mass desorbed (mg)	Percentage of metal adsorped that is desorbed
Chromium (VI)	5.5	53	21.1	0.2	0.4
	6.4	31	10.3	0.2	0.6
	7.0	21	10.4	0.5	2.4

The low level of chromium in leachate from a methanogenic landfill is not surprising. By definition, a methanogenic landfill is anaerobic, and reducing conditions are prevalent. Chromium(VI) is readily reduced to chromium(III) in the presence of organic matter, especially at low pH. The solubility of chromium(III) decreases rapidly above pH4, with complete precipitation occurring above pH5.5. There are conflicting vectors however. The presence of soluble organic acids can maintain chromium(III) in solution at pH levels above 5.5.

It is envisaged that levels of chromium in leachate from a stabilised landfill would be low, possibly lower than that from a methanogenic landfill. The complete absence of carboxylic acids, the strong fixation of chromium to municipal solid waste shown in this study, indicate a low chromium mobility. Pohland *et al* (1983) expresses concern the more microbially recalcitrant materials could produce humic-like substances which could provide soluble organic material which could then remobilise any heavy metals present. There is the possibility of the occurrence of this phenomena, but this could only occur after a number of years, or even decades.

Soil scientists have evaluated vertical chromium movement in soils. In one experiment, chromium analysis of soils, which had received metal contaminated sludge treatment from 1942 to 1961, showed no evidence of significant movement below the depth to which the soil was cultivated (McGrath *et al*, 1990). Table 6.8 reveals chromium to be one of the least mobile metals tabulated. The work of other researchers together with results obtained in this study (Table 6.10) are in agreement.

(c) Arsenic

Unfortunately the review of leachate contaminants completed by Pohland *et al* (1986b) did not include arsenic. The behaviour of arsenic is the most complex of the three metals under

consideration. The results from the kinetic trials are shown below in Table 6.11. Arsenic is well adsorbed throughout the pH range under discussion. Arsenic is also the only metal which exhibits any significant desorption.

Table 6.11 Mass and percentage of arsenic adsorbed and desorbed at pH 5.5, 6.4 and 7.0

Metal and species	pH	Average mass sorbed (mg)	Percentage adsorption	Average mass desorbed (mg)	Percentage of metal adsorped that is desorbed
Arsenic(V)	5.5	70	34.3	6	8.6
	6.4	36	20.6	4	11.1
	7.0	41	23.2	4	9.8

The mobility of arsenic in soils is increased in anaerobic conditions. This increased mobility is a consequence of the reduction of arsenic(V) to arsenic(III). Arsenic(III) is estimated to be 5 to 10 times more soluble, and hence more mobile then arsenic(V). The subject of sulphate reducing bacteria was addressed in section 2.8.2(a). Hydrogen sulphide is produced by sulphate reducing bacteria. Hydrogen sulphide is a strong reducing agent, it can react with arsenic (as with copper) causing precipitation of arsenic as insoluble arsenic sulphide. Another attenuation mechanism to consider is the co-precipitation of arsenic with iron sulphide. The iron content of leachates is generally high (see Table 6.8). Iron content is shown as low in leachate from a methanogenic landfill as a consequence of attenuation mechanisms as just discussed.

The mobility of arsenic in the acetogenic landfill and the stabilised landfill are more difficult to envisage. Some of the attenuation mechanisms available in the methanogenic landfill would not be available. As reported in section 2.8.1.3(d) there is conflicting information regarding the mobility of arsenic(III) and arsenic(V). Sadler (1993) states that arsenic(III) has a high mobility in soils; while Elkhatib and co-researchers (1984) report arsenic(III) being irreversibly sorbed by the soils examined, only a small fraction of the arsenic(III) being desorbed from the soils. Korte and co-workers (1976) concludes that arsenic(III) (however at pH3) was more mobile than other metals examined. Frost and Griffin (1977) found arsenic(V) be mobile, especially at alkaline conditions, while arsenic(III) exhibited an increase in adsorption with rising pH.

It would appear there are substantial attenuation mechanisms available to reduce the mobility of arsenic in a methanogenic landfill. Adsorption would appear to be the principal mechanism in both the acetogenic and stabilised landfill. Arsenic adsorption was satisfactory throughout the pH range under scrutiny. There would not appear to be a great deal of

difference in the behaviour of arsenic in an acetogenic landfill or that of a stabilised landfill, though adsorption of arsenic(V) is substantial at the lower pH values.

An additional problem that must be addressed when considering the co-disposal of arsenic on an acetogenic landfill is that of the generation of arsine gas (section 2.8.3(c)). Arsine (AsH_3) is an extremely poisonous gas, with no effective antidote (section 7.1). Arsine is produced whenever a reaction generating nascent hydrogen occurs in the presence of arsenic. Hydrogen can be generated in the acetogenic phase of landfill age. It is produced by hydrogen producing acetogenic bacteria (section 2.6.2). These hydrogen producing acetogenic bacteria convert the higher volatile acids to acetate and hydrogen. Pohand (1986b) reveals in Table 6.8 that hydrogen levels in gas from an acetogenic landfill have been recorded as high as 2 per cent by volume. For this reason it would appear that caution should be exercised in the co-disposal of arsenical waste in an acetogenic landfill.

(d) General

The calculations revealed that when disposing of these metals in combination the mass of copper should not exceed $67gt^{-1}$; the mass of chromium in the form of chromium(VI) should not exceed $195gt^{-1}$; the mass of arsenic should not exceed $195gt^{-1}$. A specific area which has not been addressed in the preceding section is that of the inhibiting effect of toxic industrial wastes on biological degradation of the municipal solid waste (section 2.8.3(a)). When practising co-disposal of industrial wastes with municipal solid wastes, avoidance of sterilising the landfill by exceeding the toxicity limit of the various microbial population groups and therefore inhibiting the degradation of the municipal solid waste is one of the two premier objectives. The other objective is that the emission of toxic substances in liquid and gaseous effluent from the landfill should not be greater than that from the disposal of only municipal solid waste. The latter objective was addressed in the initial assumptions of the calculation, were a worst case study was employed (section 5.4.7). The inhibition of anaerobic digestion was extensively examined in section 2.8.3(a), there is however, a number of interesting investigations deserving of further examination, for comparative purposes.

The work completed by Pohland and other workers (1985; 1986a; Gould *et al*, 1989) at the Georgia Institute of Technology, is one such study. A metal plating sludge containing zinc, chromium, nickel, cadmium, copper and iron, was co-disposed with municipal solid waste in pilot-scale landfill columns. In the control column (no addition of metal plating sludge) methanogenic conditions were established. In column 2 the onset of methanogenisis was delayed, addition of metal sludge was $84kgt^{-1}$. Where the sludge was added in a greater quantity, methanogenic conditions were not established.

Another investigation requiring further review is that undertaken by Yeates *et al* (1994). The researchers investigated the impact of copper, chromium and arsenic timber preservative on soil biological activity. Initially, the researchers visually graded areas of the pasture in terms of heavy metal contamination. Four levels of contamination were graded; uncontaminated, low contamination, medium contamination and highly contaminated. The researchers then sampled the site extensively in terms of degree of contamination and depth. The samples were then analysed for metal content and various biological parameters were measured to determine the whether there was evidence of repression of biological activities.

There was a close correlation between heavy metal contamination and the initial visual assessment. All the biological parameters measured in the contaminated area showed correlation with levels of copper, chromium and arsenic. The researchers concluded that contamination by $100mgkg^{-1}$ of copper, chromium and arsenic caused little depression of soil biological activity, there was some suppression at $400mgkg^{-1}$, but at $800mgkg^{-1}$ normal biological processes were inhibited and herbage production was negligible. These results were comparable with other workers cited by Yeates and co-researchers.

The toxicity of heavy metals in the process of anaerobic digestion is well established and has been extensively investigated by various researchers principally investigating toxicity effects in waste water anaerobic digesters. Reid and fellow researchers (1968) evaluated the effects of metallic ions on a number of biological waste treatment processes, amongst them, anaerobic digestion at laboratory scale. They found that chromium (in the form, chromium(VI)) concentrations as high as $85mg\ell^{-1}$ reduced biogas production by 18 percent, and copper when added in concentrations up to $2mg\ell^{-1}$, reduced gas production by 8 percent.

Hayes *et al* (1978) collated information concerned with the effect of metal addition on anaerobic digestion. The digesters were dosed with the metals in a step- and pulse-like fashion. Metal addition in a pulse-like mode is akin to shock loading, while metal addition in a step-like function allows microbial acclimation to the addition of the metal. The full results from the study are tabulated in Table 2.17. It was found that copper was more toxic than chromium. The shock loading toxic limit for; chromium(VI) was less than $200mg\ell^{-1}$; copper was less than $50mg\ell^{-1}$. The inhibiting concentration allowing microbial acclimation for; chromium(VI) was $110mg\ell^{-1}$; copper was $40mg\ell^{-1}$.

If one considers the work presented by Hayes and co-workers, it would appear there would not be any inhibition in anaerobic activity as the values quoted are high. Similarly, the value of $33.6kgt^{-1}$ (Pohland *et al*, 1985; Pohland *et al*, 1986a; Gould *et al*, 1989), would appear to be extremely high, a complete inhibition of anaerobic activity would have been expected, instead of only the delay of establishment of methanogenic conditions. The values presented by Reid and fellow researchers (1968) are of the same order as those presented by Hayes. Values for chromium are similar, but values presented for copper display variance. By far the most relevant of the work examined is that undertaken by Yeates and co-workers. There would appear to be some suppression at $400mgkg^{-1}$.

To fully utilise the adsorptive capacity of the municipal solid waste, it would be required to co-dispose $457gkg^{-1}$ of copper-chromium-arsenic solution. It would appear possible that the co-disposal of the copper-chromium-arsenic solution at the proposed limits in a methanogenic landfill could inhibit methanogenic activity. The work of other workers does not absolutely confirm this, but the values quoted by Reid and fellow researchers (1968) where copper when added in concentrations up to $2mg\ell^{-1}$, reduced gas production by 8 percent appear appropriate. It is conceivable that methanogenesis could be initially inhibited but it would be extremely unlikely that the anaerobic processes would not become acclimatised and proceed smoothly. This statement is confirmed by work carried out by Pohland and other researchers (1985; 1986a; Gould *et al*, 1989).

6.12 SUMMARY

The micro-physical characteristics of the metals under scrutiny, copper, chromium and arsenic were examined, and detailed. Results from the equilibrium studies were scrutinised. The Freundlich isotherm indicated the order of the degree of affinity of the metals to municipal solid waste was:

copper >> arsenic > chromium.

This was confirmed by additional graphical analysis. The effect of pH on adsorption was appraised. For all the metals under consideration the highest percentage adsorption was achieved at pH5.5 with percentage adsorption at pH6.4 and pH7.0 being similar.

Results from the kinetic trials were inspected, and reasons for the applicability of the modified Freundlich equation assessed. It was shown that diffusional effects at the solid phase were rate determining. The suitability of the Freundlich equilibrium isotherm in characterising adsorption is often taken to be indicative of adsorption onto a heterogeneous surface. Further analysis of the data showed agreement to a generalised model representative of heterogeneous adsorption. The rate of adsorption was also examined. Analysis showed the rate, and mass of adsorption increased as the initial solute concentration increased. Additionally, the rate of adsorption may be categorised in the following order:

copper >> arsenic > chromium.

Sorption mechanism was also investigated. It was evident the relative size of the ions was not the controlling mechanism, but adsorption was probably determined by electrical interaction. Tracer studies were examined, together with the pilot-scale co-disposal trials. Results from the tracer studies showed the pilot-scale column to behave as a non-ideal plug flow reactor. Results from the co-disposal trial showed good agreement with that predicted from the modelled results from the laboratory investigation. Defects in the computational method were also discussed.

The application of the pilot-scale study to a full scale landfill were discussed, in conjunction with values promulgated by the United Kingdom's Department of the Environment. Loading rates predicted by computer model were of the same order as those utilised in the United Kingdom. The final sections of the Discussion centred around the behaviour of copper, chromium and arsenic in landfills of different age together with the effect of co-disposal of those metals at the proposed loading rates on anaerobic activity.

CHAPTER 7
CONCLUSIONS

7.1 INTRODUCTION

The experimental investigation of the co-disposal of copper, chromium and arsenic is reviewed below. Individual aspects of the research are considered and relevant comments are formulated. Subsequently, possible improvements in experimental techniques are suggested, together with suggestions for further research.

7.2 EXPERIMENTAL METHODS AND EQUIPMENT

7.2.1 Laboratory scale investigation

The modification of the US EPA Method 1311 Toxicity Characteristic Leaching Procedure to determine the degree of adsorption was appropriate (section 4.5.1). The modification has the potential to be extremely useful in determining the adsorption characteristics of a number of differing industrial wastes. Similar comments could be expressed for the experimental method employed in the desorption experiments (section 4.5.2). There are a number of advantages in modifying a method developed by a major organisation such as the EPA.

(i) The method has been well researched by the EPA. By using a recognised method one is able to "piggy-back" on the research efforts of an extremely large organisation.

(ii) The extraction fluid should assimilate liquid present in a landfill. The acetic acid-sodium hydroxide-deionised water mixture should approximate the acetate buffered system. Acetic acid is the most prevalent acid intermediate formed from the fermentation of fats, carbohydrates an proteins (section 2.6.2).

(iii) Researchers and practitioners in the field of waste management are familiar with the method.

7.2.2 Pilot-scale investigation

The design of the pilot-scale columns may be considered as an improvement upon previous designs (section 4.7.1). The design of the pilot-scale columns was based upon the original design pioneered by Pohland, at the Georgia Institute of Technology. The materials and mode of construction of the pilot-scale columns constructed for this study appear superior than those previously constructed. The column shell was composed of **H**igh **D**ensity **P**oly **E**thylene (HDPE). This material has proved to be extremely durable.

The simplification of the designs of others proved to be suitable. The absence of a liquid distributor is an example of the design philosophy adopted. A layer of 6mm aggregate, of sufficient depth to ensure adequate liquid distribution was employed in this study. The sealing of the column by means of HDPE plates was also successful. The use of a U-bend on the liquid outlet of the column was another small innovation. This liquid seal prevents any ingress of oxygen while draining or sampling leachate from the column.

7.2.3 General

The strict application of the chemical engineering techniques of reactor design and transport phenomena to determine the behaviour of heavy metals in the landfill environment has proved an exciting development in landfill research. Chemical engineering techniques have proved successful in many areas of endeavour, outside the conventional areas of chemical engineering expertise.

A significant aspect of this current research was the emphasis placed upon adsorption as the only attenuation mechanism considered. Many previous researchers have concentrated upon strictly chemical affects such as reduction, precipitation, and co-precipitation. Adsorption has only been examined by a very small number of previous researchers. The emphasis upon adsorption is a worst-case examination of co-disposal. Under anaerobic conditions the other attenuation mechanisms are evident and are probably superior to adsorption in immobilising inherently non-biodegradable substances, such as heavy metals. However, if none of the other attenuation mechanisms were present, this study has shown that adsorption has the capacity to immobilise the heavy metals under consideration.

7.3 ADSORPTION EQUILIBRIUM STUDIES

Adsorption equilibrium studies and kinetic studies were undertaken at laboratory scale, at three pH values; pH5.5, pH6.4, and pH7.0. The adsorbent being municipal solid waste, the adsorbate being copper, chromium and arsenic in aqueous solution. From measurements taken at equilibrium, adsorption isotherms were constructed. Results conformed to the Freundlich isotherm. Freundlich isotherms were successfully constructed for copper at pH5.5 and 7.0; for chromium and arsenic at all three pH values mentioned previously (section 5.4.2). The results from the equilibrium studies were further examined in section 6.3. Values obtained for the Freundlich equilibrium distribution coefficient (K_F) may be considered as a measure of affinity between solute and adsorbent. Over the pH range of the laboratory studies, the degree of affinity of the metals with municipal solid waste was copper > arsenic > chromium. Additional graphical analysis was undertaken. This additional analysis confirmed the degree of affinity between solute and adsorbent indicated by the Freundlich equation.

7.4 ADSORPTION KINETIC STUDIES

The kinetic studies revealed a reaction characterised by an initial rapid adsorption rate, the rate of adsorption subsequently decreasing at larger values of time. This reaction could be successfully described by a modification of the Freundlich equation (section 5.4.4) usually termed, the modified Freundlich equation, or the two-constant equation. The modified Freundlich equation was developed by Kuo and Lotse in 1974 (section 3.3.4). Further investigation into the suitability of the modified Freundlich equation (section 6.4) revealed that it was unlikely that any of the simple kinetic models would be applicable to the adsorption of the copper-chromium-arsenic adsorption onto municipal solid waste. The use of simple rate laws assumes that only chemical kinetics are being studied and any physical aspects are being ignored (Skopp, 1986).

In section 6.5 the modified Freundlich equation was examined to determine the reason for its success in describing solid-fluid reactions. Researchers in the field of soil science have found the use of the modified Freundlich equation is indicative that reactions at the solid phase are associated with activated diffusional processes. Additional examination showed the data conformed to a generalised model indicative of heterogeneous adsorption. This confirmed earlier work, as adherence to the Freundlich isotherm is generally considered to indicate adsorption onto a heterogeneous surface.

7.5 DESORPTION KINETIC STUDIES

The desorption of chromium was insignificant, the desorption of copper was less than 4 percent of that adsorped. Arsenic desorption was more significant, it did however, average less than 10 percent of the arsenic adsorped. The analytical method employed for arsenic determination was not of sufficient sensitivity to enable the calculation of kinetic constants and could only be utilised to examine trends. As levels of desorption were relatively low, especially in the case of copper and chromium, the kinetics of desorption were not investigated further, and attention was limited to the adsorption kinetics (section 5.4.3).

7.6 PILOT-SCALE STUDIES

Five pilot-scale landfill columns were constructed. The columns are 4m in height, 0.8m in diameter, and contain approximately 700kg of municipal solid waste (section 4.7.1). The municipal solid waste was extensively sampled (section 4.3.1) and fully characterised (section 4.3.3). Analysis of the solid waste indicated the solid waste to be completely stabilised. Initially, leachate was recirculated, from all five columns to accelerate the landfill stabilisation processes (section 4.7.2 (a)). The leachate was drained, sampled, and recirculated approximately every 7 days. Analysis revealed the leachate to conform to a leachate from a fully stabilised landfill (section 5.3.1). The pilot-scale columns were also monitored for volumetric flowrate and composition of biogas. The low volumetric flowrates of biogas which after a short interval of biogas production ceased completely only served to confirm the municipal solid waste excavated from Coastal Park Sanitary Landfill Site was completely stabilised (section 4.7.2 (b); section 4.7.2 (c)).

Of the five columns only three were utilised for experimental purposes. One column (column 4) was utilised for residence time studies, while another two columns (columns 3 and 5) were employed for the co-disposal trials. As mentioned in section 4.3, it was an initial objective of the study to examine the effect of co-disposal of heavy metals with methanogenic solid waste. It was envisaged that differing quantities of CCA would be co-disposed in the pilot-scale columns to fully examine that effect. As the excavated solid waste was fully stabilised, this objective could not be met, and the two remaining columns were in excess to our requirements.

7.7 TRACER STUDIES

Tracer studies were undertaken at pilot-scale (section 4.7.3). The tracer, lithium sulphate, was firstly evaluated at laboratory scale to determine its suitability in the solid waste environment. It was found to be appropriate, being un-reactive with solid waste (section 4.7.3(a)). Tracer studies revealed (as expected) a system with conformed with a plug flow reactor, albeit with a great deal of non-ideality. This non-ideality was revealed by the tracer mass-time curve. There was evidence of:

(i) axial dispersion of the fluid;
(ii) channelling;
(iii) stagnant areas within the column.

The variance was calculated at 3338, while the mean residence time was 113 days. Maximum lithium recovery occurred after 84 days, the lithium concentration of the leachate at that time was 2.003mgℓ^{-1}. The recovery of lithium bettered 92 percent, of the 1027mg of lithium added 954mg being recovered. The pilot-scale tracer studies ceased after 317 days (section 5.4.5).

7.8 PILOT-SCALE CO-DISPOSAL STUDIES

Co-disposal experiments were then undertaken at pilot-scale. A solution of copper-chromium-arsenic was added to two of the pilot-scale columns. The effluent from the columns was closely monitored (section 5.3.3). The mass of metals introduced into both columns 3 and 5 was copper, 88.4g; chromium, 256.1g and arsenic, 256.7g. The time duration of the experiment with column 3 was 235 days, the average volumetric displacement of leachate was 19.2ℓweek^{-1}. The time duration of the experiment with column 5 was slightly shorter, 221 days. The average displacement of leachate was 18.5ℓweek^{-1}.

The initial concentration of copper in the leachate from column 3 was 0.05mgℓ^{-1}, the highest copper concentration recorded was 0.11mgℓ^{-1}. Over the entire period of monitoring (235 days), the concentration of copper in the leachate from column 3 averaged 0.05mgℓ^{-1}. The initial concentration of copper in the leachate from column 5 was 0.07mgℓ^{-1}. This value was not exceeded for the entire duration of the experiment. The final copper concentration after 221 days was 0.04mgℓ^{-1}. Over the entire period of

monitoring (221 days), the concentration of copper in the leachate from column 3 averaged 0.03mgℓ^{-1}.

Initially, chromium in the leachate from column 3 was not detectable. The chromium content of the leachate rose steadily to a maximum of 0.04mgℓ^{-1}, the final chromium concentration was 0.03mgℓ^{-1} on Day 235. The average chromium content in the leachate from column 3 over the duration of monitoring was 0.03mgℓ^{-1}. The initial chromium content of leachate from column 5 was 0.06mgℓ^{-1}, The final chromium concentration was 0.02mgℓ^{-1} on Day 221. The average chromium content in the leachate from column 5 over the duration of monitoring was 0.04mgℓ^{-1}.

The initial concentration of the arsenic in the leachate from column 3 was 17μgℓ^{-1}, rising in irregular steps to Day 194, when the concentration exceeded 2000 μgℓ^{-1}. Arsenic concentration in the leachate from column 3 remained at that level until the cessation of monitoring on day 235. Column 5 mirrored the behaviour of column 3 though at a reduced manner. The maximum arsenic concentration attained was 802μgℓ^{-1} at Day 213; results were relatively constant from Day 188 at that level.

7.9 APPLICATION OF THE LABORATORY SCALE RESULTS TO PREDICT RESULTS AT PILOT-SCALE

Conventional chemical engineering reactor design allows the computation of reactor effluent composition from results from tracer studies, in combination with kinetic results, together with details of the reactor feed (section 3.4.4). The predicted results agreed well with those obtained at pilot-scale.

The method of computation allowed representation of the results in terms of metal saturation with depth and time. Chromium almost completely saturated the column over the predicted time period. The degree of column saturation, was a consequence of the low maximum chromium equilibrium value of 0.42g of chromium per kilogram of municipal solid waste. The degree of arsenic saturation was far less than that of chromium. Arsenic only saturated approximately half the column. The equilibrium saturation concentration is high in comparison with the other metals under consideration, at 0.72gkg^{-1}. The rate of reaction is not dissimilar between chromium and arsenic. However, the high affinity of arsenic for the municipal solid waste results in far less mobility within the column.

Predicted chromium concentration in the leachate from column 3 exceeded analytical measurements (4.4mgℓ^{-1} *versus* 0.03mgℓ^{-1}). Actual arsenic concentration in the leachate from column 3 exceeded that predicted (2mgℓ^{-1} *versus* zero) (section 5.4.6(c)). Solubility restraints would have effectively immobilised any copper co-disposed with the municipal solid waste. Actual copper concentration in leachate averaged 0.05mgℓ^{-1}. The accuracy of the method of computation was examined in section 6.10. The method is rigorous and accurate at low values of time. At larger time values the degree of accuracy is lowered. A smaller depth increment would ensure that each separate time increment of fluid would not spend excessive time in each increment of depth. Thus, at large values of time it is possible the computed exit concentrations could be higher than that actually experienced.

7.10 APPLICATION OF THE LABORATORY SCALE RESULTS TO PREDICT RESULTS AT FULL SCALE

The application of the pilot-scale studies to the full scale landfill involved a worst-case study (section 5.4.7). The calculations revealed when disposing of these metals in combination, the mass of copper should not exceed $67gt^{-1}$; the mass of chromium in the form of chromium(VI) should not exceed $195gt^{-1}$; the mass of arsenic should not exceed $195gt^{-1}$. These figures reflect the distribution of the metals in solution in the copper-chromium-arsenic product. Comparison was made in section 6.11 of loading rates quoted by the DOE in the United Kingdom. They (the DOE) recommend a heavy metal loading of $100gt^{-1}$ whereas the proposed loading rate totals $262gt^{-1}$ for chromium and copper in combination.

Discussion of the loading rate quoted for arsenic was more complex. It appeared that the leachate concentration was the controlling variable. If the arsenical concentration of $10gt^{-1}$ of municipal solid waste was not exceeded, the value of $10mg\ell^{-1}$ arsenic in leachate, (recommended by the DOE) will not be exceeded. It was also evident in the case of arsenic, the DOE was extremely concerned by the possibility of the generation of arsine gas (section 2.8.3(c)). Probably, the loading rate of arsenic to be co-disposed was reduced to accommodate this problem. However, in general, loading rates proposed from the experimental work and predicted by the modelling undertaken in this study, concurred with loading rates employed in the United Kingdom, recommended by the Department of the Environment.

In section 6.11.1 the behaviour of the metals was examined in terms of the different stages of landfill life. Data and information compiled by other researchers was scrutinised. It was envisaged that copper would be immobile whether co-disposed in an acetogenic, methanogenic, or stabilised landfill. Data collated by Pohland (1986b) indicated that copper would be immobile in a methanogenic and a stabilised landfill. Mobility of copper would be greatest in an acetogenic landfill. It was envisaged that mobility of chromium would be limited whether co-disposed in an acetogenic, methanogenic, or stabilised landfill. Examination of the work of other researchers indicated that chromium would be immobile in a methanogenic and a stabilised landfill. Mobility of chromium would be greatest in an acetogenic landfill. It is probable that soluble organic acids enhance the mobility of chromium in an acetogenic landfill. The behaviour of arsenic was also examined in terms of co-disposal in landfills of different ages. Although this study revealed good adsorption of arsenic at low pH levels it would appear unwise to co-dispose arsenic in an acetogenic landfill. A consequence could be the generation of arsine gas (section 2.8.3(c)). The effect of co-disposal of the metals (at the proposed levels) on anaerobic activity was also examined. There would appear to be a possibility that anaerobic activity could be retarded until acclimation of the anaerobic microbes occurred. Subsequently, it is envisaged that anaerobic digestion would proceed unhampered.

7.11 SIGNIFICANCE OF THE WORK UNDERTAKEN IN THIS INVESTIGATION

The chemicals under discussion, by their very nature, and their toxicity to living organisms, can be hazardous to personnel handling them, the general public should they inadvertently come into contact with them, and to the environment at large. The disposal of copper-chromium-arsenic whether in solution or in combination with wood has the potential to become a global problem (section 2.11 and section 2.12). The total production of the various chemicals used for wood preservation is estimated to be excess of 550 000 tonnes per annum. The copper-chromium-arsenic wood preservative is classed as a waterborne preservative. Current production is estimated at 90 000 tonnes per annum. In South Africa (1988) the production of preservative treated wood approximates 430 000 $m^3 annum^{-1}$.

As reported in section 2.11, the **I**ndustry and **E**nvironmental **P**rogramme **A**ctivity **C**entre (IEPAC) operating under the umbrella of the United Nations is concerned about the disposal of treated timber (UNEP, 1994). The amount of timber being treated globally continues to rise, at present over 30 million cubic metres of wood are being industrially treated, and after 30 years, disposal will then be required. The IEPAC comments that current disposal options are not encouraging, uncontrolled burning is *out of the question*, incineration of such volumes *impractical*, and disposing to landfill is *not encouraging*. It is of great importance that investigations such as this are completed to ensure materials such as this and similar materials are disposed of in a responsible manner, with minimal environmental damage. If industrial wastes or even general wastes are disposed to landfill, the wastes must be securely bound within that landfill, without the potential to provide environmental damage in future decades.

Additional significance is given to this research, as the issue of co-disposal of hazardous waste with non-hazardous waste is under close scrutiny in Europe. In United Kingdom the practice of co-disposal is strongly supported by the Department of the Environment. However, the present text, of the proposed European Community Landfill Directive would prohibit the establishment of new co-disposal landfill sites. Nevertheless, co-disposal will continue to be practised in the United Kingdom on suitable existing landfill sites (DETR, 1996).

7.12 PROPOSALS FOR FURTHER RESEARCH

This study has examined the co-disposal of copper, chromium, and arsenic in solution. Overall, the method utilised to define loading rates of copper-chromium-arsenic onto municipal solid waste has proved to be suitable. It would be advantageous to maintain the laboratory scale experimental method and determine the adsorption characteristics of other industrial wastes. Various other heavy metals should be examined in combination (as in this study), and individually.

The use of the large pilot-scale columns employed in this study would not be warranted for further research. Municipal solid waste proved to be far more homogenous than

initially suspected. Though, as mentioned previously (section 4.3.1), the sampling programme included in this investigation was exhaustive. The municipal solid waste was subjected to size reduction prior to sampling and placing in the pilot-scale columns. This action improved the homogeneity of the solid waste. This would allow the use of smaller columns. The use of smaller columns would accelerate the experimental programme to more acceptable time-frames.

The philosophy of the computational method of modelling the laboratory scale results proved to be pertinent. Minor difficulties experienced with the modelling of the kinetic constants obtained at laboratory scale (section 6.10) could easily be alleviated by modest adjustments.

Throughout this investigation the *scenario* of worst case conditions has been implemented. The landfill has been considered to be at field capacity to conform to that philosophy. An interesting aspect worthy of further research is unsaturated flow in the landfill environment. This would realise more representative conditions, especially in South Africa, with its varying weather conditions. However, probably the most important matter requiring further research when considering the co-disposal of heavy metals with municipal solid waste is the possible remobilisation of heavy metals. This concern is also relevant when considering domestic refuse; heavy metal levels in domestic refuse cannot be considered negligible (Table 4.2). It would appear unlikely that metals adsorbed onto municipal solid waste would be remobilised. This study examined possible desorption with an acetic acid based extraction fluid (section 4.5.2). However, an attenuation mechanism often mentioned, is that of precipitation. It would appear possible for precipitated metals to be remobilised with possible subsequent environmental damage.

7.13 SUMMARY

Experimental methods and equipment have been reviewed. In general, these were thought to be pertinent, though it was not recommended to construct smaller columns for future research. Data generated by the equilibrium studies conformed to the Freundlich Isotherm; the kinetic studies were described by a modification of the Freundlich equation. Adherence to these equations, is indicative of heterogeneous adsorption. Additionally, it was shown that diffusional constraints were evident.

Lithium sulphate was shown, at both laboratory and pilot-scale, to be a suitable tracer in the landfill environment. Results from the co-disposal trials indicated that the residence time trials and the kinetic studies had been well administered. Agreement between the co-disposal trials and that predicted from the trials was excellent. The application of the pilot-scale results to the full scale landfill demonstrated when disposing copper-chromium-arsenic in combination, the mass of copper should not exceed $67gt^{-1}$; the mass of chromium in the form of chromium(VI) should not exceed $195gt^{-1}$; the mass of arsenic should not exceed $195gt^{-1}$. These figures reflect the distribution of the metals in solution in the copper-chromium-arsenic product.

The matter of further research was also examined. It is considered that the most important matter requiring further research with regard to the co-disposal of heavy metals with municipal solid waste and the disposal of domestic refuse, is the possible remobilisation of heavy metals.

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APPENDIX A

United States Environmmental Protection Agency Method 1311 Toxicity Characteristic Leaching Procedure.

The US EPA Method 1311 Toxicity Characteristic Leaching Procedure, for non-volatile solid wastes, and the required equipment, is summarised below.

Scope and application
The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid and multi-phasic wastes.

Apparatus and materials
Agitation apparatus: The agitation apparatus must be capable of rotating the extractor vessel in an end-over-end fashion at 30 (+/- 2) rpm.
Bottle Extractor vessel: A jar of sufficient capacity to hold the sample and the extraction fluid is required. Provision for headspace is needed in the extractor vessel.
pH meter: The pH meter should be accurate to +/- 0.05 units at 25°C.
Laboratory Balance: Any laboratory balance accurate to within +/- 0.01g may be used (all weight measurements are to be within +/- 0.1g).
Beaker or Erlenmeyer flask, glass, 500 mℓ.
Magnetic stirrer.

Reagents
It is a requirement that reagent grade chemicals to be used in all aspects of the test. The required reagents are detailed below.
1. Distilled or deionised water (reagent water).
2. Hydrochloric acid (1 N)
3. Sodium hydroxide (1 N)
4. Glacial acetic acid.

Preparation of the extraction fluids
The extraction fluid employed is a function of the alkalinity of the solid phase of the waste

Extraction fluid #1:
Extraction fluid #1 is prepared as detailed below.

> Add 5.7 mℓ glacial acetic acid to 500 mℓ of reagent water, mix well. Add 64.3 mℓ of 1 N sodium hydroxide, and dilute to a volume of 1ℓ.

If correctly prepared, the pH of this fluid will be 4.93 +/- 0.05.

Extraction fluid #2:
Extraction fluid #2 is prepared as detailed below.

> Dilute 5.7 mℓ glacial acetic acid with reagent water to a volume of 1ℓ.

If correctly prepared, the pH of this fluid will be 2.88 +/- 0.05.

United States Environmmental Protection Agency Method 1311 Toxicity Characteristic Leaching Procedure.

The US EPA Method 1311 Toxicity Characteristic Leaching Procedure, for non-volatile solid wastes, and the required equipment, is summarised below.

Scope and application
The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid and multi-phasic wastes.

Apparatus and materials
Agitation apparatus: The agitation apparatus must be capable of rotating the extractor vessel in an end-over-end fashion at 30 (+/- 2) rpm.
Bottle Extractor vessel: A jar of sufficient capacity to hold the sample and the extraction fluid is required. Provision for headspace is needed in the extractor vessel.
pH meter: The pH meter should be accurate to +/- 0.05 units at 25°C.
Laboratory Balance: Any laboratory balance accurate to within +/- 0.01g may be used (all weight measurements are to be within +/- 0.1g).
Beaker or Erlenmeyer flask, glass, 500 mℓ.
Magnetic stirrer.

Reagents
It is a requirement that reagent grade chemicals to be used in all aspects of the test. The required reagents are detailed below.
1. Distilled or deionised water (reagent water).
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Extraction fluid #1:
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If correctly prepared, the pH of this fluid will be 4.93 +/- 0.05.

Extraction fluid #2:
Extraction fluid #2 is prepared as detailed below.

> Dilute 5.7 mℓ glacial acetic acid with reagent water to a volume of 1ℓ.

If correctly prepared, the pH of this fluid will be 2.88 +/- 0.05.

Procedure

Firstly, visually examine the waste, there are three requisites. The waste must be free of extraneous liquid; the particle size of the waste should meet the requirements of the method (see below); the analyst must determine which of the two extraction fluids are to be used for the TCLP extraction.

Determination of whether the waste requires particle size reduction

Particle size reduction will be required, unless the solid has a surface area per gram greater or equal to 33.1 cm^2, or is smaller than 1 cm in its narrowest dimension. The material should be capable of passing through a 9.5 mm (0.375 inch) standard sieve.

Determination of appropriate extraction fluid

Weight out a small sub-sample of the waste, reduce the solid (if necessary) to a particle size of approximately 1 mm in diameter or less, and transfer 5.0g of the waste to a 500 mℓ beaker or Erlenmeyer flask. Add 96.5 mℓ of the reagent water to the beaker, cover with a watchglass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is less than 5.0 use extraction fluid #1. If the pH is greater than 5.0 add 3.5 mℓ of 1 N hydrochloric acid, slurry briefly, cover with a watchglass, heat to 50°C, and hold at 50°C for 10 minutes. Let the solution cool to room temperature and record the pH. If the pH is less than 5.0, use extraction fluid #1. If the pH is greater than 5.0, use extraction fluid #2.

Extraction method

A minimum sample size of 100g is recommended. Weight and record the mass of the sample. Transfer the sample into an extractor bottle. Determine the amount of extraction fluid to be added to the extractor vessel as follows:

Weight of extraction fluid = (20 x weight of waste)

Slowly add the calculated amount of the appropriate extraction fluid to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal), secure the extractor bottle in the rotary agitation device, and rotate at 30 (+/- 2) rpm for 18 (+/- 2) hours. The ambient temperature of the room in which the extraction takes place should be maintained at 23 (+/- 2) °C during the extraction procedure. Following the 18 (+/- 2) hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtration. The filtrate is termed the TCLP extract. Immediately following the collection of the TCLP extract, the pH should be recorded. Finally, without delay, aliquot and preserve the extract for analysis.

APPENDIX B

Table B-1
Equilibrium adsorption studies at pH 5.5

Code	Time(h)	Copper ($mg\ell^{-1}$)	Total Chromium ($mg\ell^{-1}$)	Total Arsenic ($mg\ell^{-1}$)
A	0.0	63.6	263	255
	32.0	8.8	221	163
B	0.0	53.2	265	231
	32.0	8.4	217	194
C	0.0	65.1	263	260
	32.0	11.9	196	179
N	0.0	60.0	283	273
	32.0	6.7	216	165
X	0.0	49.4	170	198
	32.0	5.2	143	121
Y	0.0	36.0	126	145
	32.0	3.8	102	92
Z	0.0	14.5	54	64
	32.0	1.7	38	37

Table B-2
Equilibrium adsorption studies at pH 6.4

Code	Time (h)	Copper ($mg\ell^{-1}$)	Total Chromium ($mg\ell^{-1}$)	Total Arsenic ($mg\ell^{-1}$)
D	0.0	9.6	269	228
	32.0	1.3	234	187
E	0.0	14.4	262	225
	32.0	2.5	230	191
F	0.0	21.3	259	231
	32.0	0.3	232	197
P	0.0	7.3	286	234
	32.0	3.1	263	195
U	0.0	7.7	172	185
	32.0	2.0	159	143
V	0.0	8.8	120	122
	32.0	2.6	109	93
W	0.0	11.7	51	57
	32.0	2.0	45	38

Table B-3
Equilibrium adsorption studies at pH 7.0

Code	Time (h)	Copper ($mg\ell^{-1}$)	Total Chromium ($mg\ell^{-1}$)	Total Arsenic ($mg\ell^{-1}$)
G	0.0	30.8	223	238
	32.0	3.5	203	186
H	0.0	22.1	224	219
	32.0	2.9	202	183
I	0.0	27.4	230	214
	32.0	5.0	209	178
Q	0.0	6.2	232	196
	32.0	0.9	215	169
R	0.0	4.9	175	185
	32.0	1.7	156	143
S	0.0	7.5	126	131
	32.0	1.4	105	90
T	0.0	4.5	50	56
	32.0	1.6	45	34

Table B-4
Kinetic studies: adsorption at pH 5.5

Code	Time (h)	Copper ($mg\ell^{-1}$)	Total Chromium ($mg\ell^{-1}$)	Total Arsenic ($mg\ell^{-1}$)
A	Initial solution	80.4	271	266
	0.0	63.6	263	255
	0.5	20.4	245	211
	1.0	14.3	249	195
	2.0	15.5	237	206
	4.0	12.2	248	137
	8.0	6.2	235	186
	16.0	10.5	230	178
	32.0	8.8	221	163
B	Initial solution	81.4	275	254
	0.0	53.2	265	231
	0.5	25.5	247	203
	1.0	17.5	246	209
	2.0	14.9	246	193
	4.0	14.2	248	132
	8.0	16.2	234	224
	16.0	4.8	228	208
	32.0	8.4	217	194
C	Initial solution	79.1	271	291
	0.0	65.1	263	260
	0.5	23.5	239	239
	1.0	23.0	241	233
	2.0	19.0	231	222
	4.0	17.3	241	220
	8.0	12.1	227	192
	16.0	7.7	216	183
	32.0	11.9	196	179

Table B-5
Kinetic studies: adsorption at pH 6.4

Code	Time (h)	Copper ($mg\ell^{-1}$)	Total Chromium ($mg\ell^{-1}$)	Total Arsenic ($mg\ell^{-1}$)
D	Initial solution	78.9	273	283
	0.0	9.6	269	228
	0.5	3.9	244	207
	1.0	2.2	254	215
	2.0	1.4	253	215
	4.0	3.0	243	202
	8.0	2.0	243	201
	16.0	1.6	239	191
	32.0	1.3	234	187
E	Initial solution	80.5	270	274
	0.0	14.1	262	225
	0.5	3.3	241	207
	1.0	0.8	243	201
	2.0	2.0	245	216
	4.0	1.3	241	216
	8.0	2.1	240	207
	16.0	0.7	238	193
	32.0	2.5	230	191
F	Initial solution	80.6	271	284
	0.0	21.3	259	231
	0.5	6.1	243	217
	1.0	3.1	246	213
	2.0	3.7	243	209
	4.0	1.8	242	205
	8.0	1.1	240	200
	16.0	0.5	238	206
	32.0	0.3	232	197

Table B-6
Kinetic studies: adsorption at pH 7.0

Code	Time (h)	Copper ($mg\ell^{-1}$)	Total Chromium ($mg\ell^{-1}$)	Total Arsenic ($mg\ell^{-1}$)
G	Initial solution	80.1	264	278
	0.0	30.8	223	238
	0.5	4.3	210	203
	1.0	3.5	209	196
	2.0	4.4	213	195
	4.0	1.1	211	184
	8.0	2.6	206	178
	16.0	5.3	205	186
	32.0	3.5	203	186
H	Initial solution	80.2	269	268
	0.0	22.1	224	219
	0.5	8.8	212	204
	1.0	6.1	213	198
	2.0	6.3	210	195
	4.0	3.8	213	190
	8.0	4.2	208	193
	16.0	3.4	204	192
	32.0	2.9	202	183
I	Initial solution	79.7	269	286
	0.0	27.4	230	214
	0.5	6.6	219	204
	1.0	4.3	217	191
	2.0	3.1	214	190
	4.0	2.4	219	191
	8.0	4.6	213	173
	16.0	1.0	207	179
	32.0	5.0	209	178

Table B-7
Kinetic studies: desorption at pH 5.5

Code	Time (h)	Copper ($mg\ell^{-1}$)	Total Chromium ($mg\ell^{-1}$)	Total Arsenic ($mg\ell^{-1}$)
A	0.0	0.2	0.0	0
	0.5	3.1	0.2	6
	1.0	3.9	0.3	4
	2.0	2.9	0.2	6
	4.0	3.1	0.4	5
	8.0	1.4	0.2	5
	16.0	2.7	0.2	5
	32.0	2.6	0.2	7
B	0.0	0.2	0.0	0
	0.5	4.8	0.4	4
	1.0	3.9	0.2	4
	2.0	2.7	0.2	4
	4.0	2.7	0.1	3
	8.0	4.0	0.3	6
	16.0	1.6	0.1	4
	32.0	1.5	0.3	6
C	0.0	0.1	0.1	0
	0.5	1.7	0.3	1
	1.0	2.9	0.5	4
	2.0	2.4	0.3	5
	4.0	3.2	0.5	9
	8.0	1.9	0.2	4
	16.0	1.4	0.3	5
	32.0	1.7	0.2	6

Table B-8
Kinetic studies: desorption at pH 6.4

Code	Time (h)	Copper ($mg\ell^{-1}$)	Total Chromium ($mg\ell^{-1}$)	Total Arsenic ($mg\ell^{-1}$)
D	0.0	0.1	0.0	0
	0.5	0.6	0.3	1
	1.0	0.6	0.3	2
	2.0	0.8	0.4	1
	4.0	0.4	0.2	2
	8.0	0.6	0.3	3
	16.0	0.6	0.3	3
	32.0	0.4	0.2	4
E	0.0	0.0	0.0	0
	0.5	0.3	0.1	0
	1.0	0.3	0.1	0
	2.0	0.4	0.1	1
	4.0	0.5	0.2	4
	8.0	0.3	0.2	0
	16.0	0.5	0.2	2
	32.0	0.5	0.2	3
F	0.0	0.0	0.0	0
	0.5	0.3	0.1	1
	1.0	0.5	0.1	1
	2.0	0.8	0.2	2
	4.0	0.5	0.1	2
	8.0	0.9	0.2	3
	16.0	0.6	0.2	2
	32.0	0.7	0.2	4

Table B-9
Kinetic studies: desorption at pH 7.0

Code	Time (h)	Copper ($mg\ell^{-1}$)	Total Chromium ($mg\ell^{-1}$)	Total Arsenic ($mg\ell^{-1}$)
G	0.0	0.1	0.0	0
	0.5	0.8	0.1	1
	1.0	0.6	0.1	0
	2.0	1.1	0.1	0
	4.0	1.3	0.2	0
	8.0	1.1	0.2	3
	16.0	1.3	0.3	2
	32.0	0.8	0.2	5
H	0.0	0.1	0.0	0
	0.5	0.4	0.2	0
	1.0	0.9	0.2	0
	2.0	0.9	0.2	0
	4.0	0.6	0.1	2
	8.0	0.7	0.1	3
	16.0	1.1	0.2	2
	32.0	1.0	0.2	3
I	0.0	0.1	0.0	0
	0.5	0.6	0.3	0
	1.0	0.8	0.3	2
	2.0	0.9	0.4	2
	4.0	0.8	0.4	4
	8.0	0.9	0.4	5
	16.0	0.9	0.5	4
	32.0	0.9	1.1	4

APPENDIX C

Pilot-scale studies: Leachate recirculation

The following nomenclature is employed in the tabulated results.

Electrical conductivity:	Elect. Cond.	(mSm^{-1})
Chemical **O**xygen **D**emand (COD), unfiltered:	COD(uf)	($mg\ell^{-1}$)
Chemical **O**xygen **D**emand (COD), filtered:	COD(f)	($mg\ell^{-1}$)
Chloride content:	Cl^-	($mg\ell^{-1}$ as Cl^-)
Total Alkalinity:	TA	($mg\ell^{-1}$ as $CaCO_3$)
Bicarbonate Alkalinity:	BA	($mg\ell^{-1}$ as $CaCO_3$)
Volatile acid Alkalinity	Va A	($mg\ell^{-1}$ as $CaCO_3$)
Orthophosphate:	OP	($mg\ell^{-1}$ as P)
Volume of leachate drained:	Vol	(ℓ)

Table C-1
Pilot-scale landfill column Number 1

Day	pH	Elect. Cond.	COD (uf)	COD (f)	Cl^-	TA	BA	Va A	OP	Vol
60	7.2	506	3440		1800	3900				60
67	7.0	572	4724		1500	4450				33
74	7.0	360	4627		1200	4400				34
83	7.1	266	3744	2701	1100	4400			1.3	31
89	7.0	373	2964	2078	1000	4339	3762	577	8.0	30
96	7.3	467	2624	2128	1000	4138	3736	402	1.0	30
103	6.8	550	2437	1934	1000	3874	3630	244	1.2	28
110	7.0	467	1768	1602	1000	3941	3641	299	0.1	33
118	6.9	960	2036	1740	950	4015	3748	267	0.2	35
231	6.7	980	1692	1194	1000	4079	3904	175	7.6	36
238	6.9	1010	1771	1293	1090	4182	3876	306	0.2	29
245	6.8	1060	1788	1623	990	4257	3858	398	4.5	26
252	7.0	940	1859	1434	1050	4307	4064	243	0.01	38
259	7.0	1220	1729	1250	1010	4266	3893	373	0.7	28
266	6.6	1210	1785	1733	1000	4046	3639	407	2.0	32
274	6.8	1120	1990	1424	1040	4054	3903	151	2.8	36
280	6.9	1150	1598	1464	1005	4041	3615	426	1.0	31
287	6.8	920	1635	1350	1020	3978	3696	281	0.2	30
294	7.0	1100	1576	1455	1005	3938	3563	375	0.4	22
301	7.1	1130	1508	1319	1070	4125	3749	376	0.7	32
308	7.2	920	1388	1122	1010	3943	3562	381	1.8	29
316	7.0	1140	1395	1336	1000	2371	2067	304	1.0	27
322	7.0	1060	1455	1215	1035	4216	3877	339	0.1	27
329	7.0	1120	1464	1352	1075	3961	3608	352	0.1	26
337	6.8	1170	1463	1427	1015	3817	3320	497	0.2	24
343	7.1	950	1455	1248	1085	3909	3840	69	0.1	45
350	7.0	1030	1374	1252	1025	2698	2406	292	0.1	24
358	6.9	1060	1354	1323	1070				0.1	82

Table C-2
Pilot-scale landfill column Number 2

Day	pH	Elect. Cond.	COD (uf)	COD (f)	Cl^-	TA	BA	Va A	OP	Vol
60	7.1	453	6209		2100	4500				65
67	7.1	541	6717		1800	4800				40
74	7.0	257	6020		1400	4550				36
83	7.2	258	4103	3049	1200	4600			4.0	32
89	7.2	356	3514	2522	1350	4838	4285	553	3.0	35
96	7.2	415	3020	1901	1150	4406	4106	301	1.0	33
103	7.1	499	2944	2684	1050	4181	3815	366	1.0	31
110	7.0	452	1919	1592	1000	4044	3739	305	0.1	30
118	6.9	970	2494	2107	1050	4098	3773	325	0.1	27
231	6.8	1060	1990	1433	1060	4154	3782	372	11.4	34
238	6.8	1030	2005	1732	1110	4228	3899	329	0.3	30
245	6.8	1130	1953	1695	1050	4290	4027	263	2.0	34
252	6.9	720	2000	1475	1070	4387	4089	298	0.3	33
259	7.0	1430	1854	1729	1040	4355	4001	354	0.8	48
266	6.8	1220	1723	1590	1070	4262	4060	202	2.8	61
274	7.0	1270	1780	1634	1050	3836	3511	325	2.7	45
280	6.9	1050	1649	1515	1035	4068	3781	287	0.8	38
287	6.9	900	1635	1482	1090	3841	3596	244	0.2	60
294	7.0	950	1646	1465	1045	3906	3617	290	1.7	25
301	7.1	1090	1634	1382	1100	3980	3725	255	2.2	57
308	7.3	900	1469	1265	1050	3868	3583	284	2.0	43
316	7.0	1170	1322	1233	1050	2508	2235	273	0.2	47
322	7.1	1040	1472	1384	1115	3922	3588	333	0.1	27
329	7.0	1090	1427	1352	1075	3741	3475	267	0.2	27
337	6.9	1140	1372	1309	1055	3676	3305	371	0.2	44
343	7.1	890	1426	1287	1060	3662	3335	327	0.1	26
350	7.1	960	1394	1272	1050	3135	2819	316	0.0	79
358	7.0	910	1375	1260	1050				0.1	27

Table C-3
Pilot-scale landfill column Number 3

Day	pH	Elect. Cond.	COD (uf)	COD (f)	Cl^-	TA	BA	Va A	OP	Vol
60	7.1	366	3043		1800	3800				60
67	7.1	541	6717		1800	4800				53
74	7.0	301	4527		1250	4200				50
83	7.1	223	3590	2997	1200	4200			7.2	48
89	7.1	307	3307	2801	1050	4235	3690	545	7.7	40
96	7.0	364	3020	2099	1050	4056	3670	387	1.1	38
103	7.1	441	2944	2380	1000	4010	3666	344	0.2	32
110	7.0	312	2020	1985	1000	4053	3795	258	0.1	34
118	6.9	940	2199	1668	1000	4042	3691	351	0.2	33
231	6.8	1070	1811	1512	980	4116	3784	331	14.4	28
238	6.8	1010	1995	1691	1020	4214	3887	327	11.3	41
245	6.8	1100	1871	1561	960	4292	4075	2107	0.4	39
252	6.8	1090	1798	1414	990	4296	3996	300	0.3	36
259	7.1	1290	1875	1063	950	4274	3960	314	0.7	32
266	6.8	1150	1713	1549	940	4160	3731	430	2.0	38
274	7.0	1100	1598	1144	940	4100	3566	534	3.9	37
280	6.9	1120	1608	1423	935	4111	3846	265	1.0	38
287	7.0	870	1574	1350	955	4003	3670	333	0.2	34
294	7.1	960	1545	1424	955	4075	3799	276	2.5	30
301	7.2	880	1445	1277	1000	4088	39.5	182	2.7	33
308	7.1	970	1388	1224	1000	4051	3763	288	1.4	34
316	6.9	1190	1116	1099	970	2627	2372	255	1.6	29
322	7.1	1030	1455	1233	955	4167	3985	272	0.1	27
329	7.0	1140	1464	1287	965	3969	3659	310	0.1	30
337	6.9	1080	1436	1264	945	4102	3789	313	0.2	30
343	7.1	880	1475	1277	995	3943	3638	305	0.3	31
350	7.1	920	1364	1242	950	3602	3390	211	0.3	35
358	7.0	950	1323	1219	950				0.2	28

Table C-4
Pilot-scale landfill column Number 5

Day	pH	Elect. Cond.	COD (uf)	COD (f)	Cl^-	TA	BA	Va A	OP	Vol
60	7.1	346	2300		1600	4000				60
67	7.1	364	3184		1300	4300				44
74	7.0	284	3582		1250	4050				40
83	7.1	208	3128	2271	1100	4150			6.0	49
89	7.1	287	3264	2491	1150	4143	3804	339	7.5	29
96	7.0	341	2723	2394	1050	3928	3585	343	7.5	28
103	7.1	386	2437	2157	1100	3825	3521	304	0.2	26
110	7.0	313	2020	1683	1000	3832	3566	266	1.5	30
118	6.9	910	2494	2107	1000	3900	3564	336	1.9	13
231	6.8	960	1930	1532	1060	3951	3525	426	8.1	31
238	6.8	980	1975	1670	1040	4097	3737	361	14.6	40
245	6.9	1050	1840	1488	1050	4141	3793	348	0.0	21
252	6.8	1110	1859	1394	870	4184	3881	303	0.1	33
259	7.0	1340	1646	1396	980	4254	4023	232	3.0	30
266	6.8	1140	1621	1477	965	4019	3643	377	2.8	37
274	7.0	1170	1613	1424	100	4075	3624	451	3.5	38
280	6.9	940	1464	1351	965	3973	3749	224	1.0	31
287	7.0	740	1452	1310	1020	3915	3548	367	0.1	29
294	7.1	880	1455	1283	980	3905	3640	264	2.2	22
301	7.2	870	1361	1215	1010	4022	3749	273	2.9	32
308	7.2	1050	1408	1286	1040	4089	3851	239	2.2	20
316	6.9	1260	1175	998	1000	2472	2250	222	0.2	20
322	7.0	1000	1455	1144	990	4020	3760	260	0.1	27
329	7.0	1150	1361	1221	995	3907	3681	225	0.8	24
337	6.9	1040	1309	1219	980	3932	3636	296	0.2	28
343	7.1	970	1366	1158	1025	3816	3568	249	0.1	45
350	7.0	930	1547	1160	1000	3775	3371	405	0.1	36
358	7.0	970	1281	1125	990				0.1	59

Table C-5
Pilot-scale landfill column Number 4

Day	pH	Elect. Cond.	COD (uf)	COD (f)	Cl^-	TA	BA	Va A	OP	Vol
60	7.1	311	2300		1300	3150				90
67	7.0	356	441		1200	4200				37
74	6.9	264	4279		1200	4000				37
83	7.1	207	3897	2752	1100	4100			7.4	40
89	7.1	284	3036	2605	1000	4139	3665	474	6.1	30
96	7.0	336	2574	2089	1000	4033	3701	333	3.5	34
103	7.1	410	2335	2137	1000	3878	3595	283	0.7	30
110	7.0	358	2020	1985	1050	3904	3635	268	0.2	32
118	6.9	910	2392	2025	1000	3948	3662	286	0.2	20

APPENDIX D

Table D-1
Results from Lithium sulphate pulse experiment: volumetric flowrate and lithium concentration: column 4

Day (tracer)	Lithium concentration ($mg\ell^{-1}$)	Volumetric flowrate (ℓ)	Lithium mass (mg)	Lithium cumulative mass (mg)
0	0.034	33	1.122	1.122
7	0.035	34	1.190	2.312
14	0.052	27	1.404	3.716
21	0.140	32	4.480	8.196
29	0.295	37	10.915	19.111
35	0.372	34	12.648	31.759
42	0.542	37	20.054	51.813
49	0.801	31	24.831	76.644
56	1.242	31	38.502	115.146
63	1.284	37	47.508	162.654
70	1.950	35	68.250	230.904
77	1.976	37	73.112	304.016
84	2.003	38	76.114	380.130
92	1.820	39	70.980	451.110
98	1.701	38	64.638	515.748
106	1.427	40	57.080	572.828
112	1.218	36	43.848	616.676
119	1.118	34	38.012	654.688
126	1.021	35	35.735	690.423
134	0.697	36	25.092	715.515
140	0.682	33	22.506	738.021
147	0.624	34	21.216	759.237
155	0.539	32	17.248	776.485
161	0.490	35	17.150	793.635

Day	Lithium concentration ($mg\ell^{-1}$)	Volumetric flowrate (ℓ)	Lithium mass (mg)	Lithium cumulative mass (mg)
168	0.456	32	14.592	808.227
176	0.422	32	13.504	821.731
183	0.364	32	11.648	833.379
190	0.469	34	15.946	849.325
197	0.435	33	14.355	863.680
204	0.379	33	12.507	876.187
211	0.266	35	9.310	885.497
218	0.172	43	7.396	892.893
224	0.209	34	7.106	899.999
234	0.145	44	6.380	906.379
239	0.145	40	5.800	912.179
246	0.140	40	5.600	917.779
253	0.125	38	4.750	922.529
260	0.120	35	4.200	926.729
267	0.108	37	3.996	930.725
274	0.099	40	3.960	934.685
281	0.094	41	3.854	938.539
288	0.094	37	3.478	942.017
295	0.089	38	3.382	945.399
302	0.081	43	3.483	948.882
309	0.074	38	2.812	951.694
317	0.068	38	2.584	954.278
	Ave. flowrate	5.211 $Lday^{-1}$		

Note
Day 0 corresponds to Day 182 in the overall experiment
The initial mass of lithium sulphate added = 1027.7 mg

Table D-2
Associated chemical analysis of the leachate from column 4

Day	Day (tracer)	pH	Elect. Cond.	COD (uf)	COD (f)	Cl^-	TA	BA	Va A	OP
182	0	6.8	1078	1955	1357	920	3927	3654	273	0.1
189	7	6.9	1091	2040	1949	920	4023	3655	368	0.2
196	14	6.7	1047	2030	1970	920	4170	3744	426	4.1
203	21	6.8	1130	2020	1929	925	4040	3671	369	11.8
210	28	6.3	1060	1959	1867	920	3080	2745	334	10.5
217	35	6.9	1040	1990	1789	915	3588	3082	506	9.0
224	42	6.8	1080	1689	1617	920	3651	3324	327	3.9
231	49	6.8	960	1532	1134	850	4090	3733	357	105
238	56	6.8	910	1466	1083	930	4063	3855	208	6.9
245	63	6.9	960	1293	1010	750	3896	3696	201	0.0
252	70	6.8	730	1273	929	620	3697	3422	275	0.03
259	77	7.2	1220	1083	750	480	3267	3102	165	3.1
266	84	6.9	790	954	749	400	2991	2909	82	1.6
274	92	7.0	590	817	607	310	2632	2470	161	4.4
280	98	6.9	530	619	577	270	2589	2484	105	0.4
287	105	6.9	540	548	528	240	2364	2244	121	0.2
294	112	7.1	430	525	475	200	2364	2224	141	0.8
301	119	7.3	470	458	375	190	2359	2136	223	0.7
308	126	7.2	460	449	388	170	2240	2099	142	1.3
316	134	6.9	560	457	423	145	1441	1324	117	0.1
322	140	7.1	450	465	425	130	2234	2070	164	0.1
329	147	6.9	450	457	401	110	2007	1794	213	0.1
337	155	6.7	450	470	433	90	2076	1936	139	0.3
343	161	7.0	510	515	347	110	1926	1819	107	0.1
350	168	7.1	360	392	336	70	1848	1693	155	0.1
358	176	6.8	448	281	65	-	-	-	-	0.1
365	183	6.7	370	232	212	140	1781	1670	111	0.0
372	190	6.6	370	478	234	100	1799	1724	55	0.3
379	197	6.6	330	226	205	100	1764	1653	112	0.1

Day	Day (tracer)	pH	Elect. Cond.	COD (uf)	COD (f)	Cl^-	TA	BA	Va A	OP
386	204	6.8	430	216	155	60	1733	1529	203	0.0
393	211	6.5	320	297	249	50	1324	1273	51	0.1
400	218	6.4	220	253	223	40	1125	1056	69	0.5
406	224	6.2	260	140	90	48	1049	1048	1	0.1
416	234	6.5	250	259	183	35	1104	1101	3	0.1
421	239	6.4	230	218	169	30	990	908	83	0.1
428	246	6.6	290	197	187	30	1198	1137	60	0.1
435	253	7.5	240	198	125	40	1370	123	247	0.1
442	260	6.9	230	185	138	50	958	957	1	0.1
449	267	6.3	250	171	160	30	940	939	2	0.0
456	274	6.5	230	355	254	40	960	940	20	0.0
463	281	6.3	350	163	117	60	869	846	24	0.1
470	288	6.6	460	204	81	90	-	-	-	-
477	295	6.5	200	133	92	30	-	-	-	-
484	302	6.8	190	121	100	40	-	-	-	-
491	309	6.7	190	123	103	50	-	-	-	-
499	317	6.6	330	340	144	55	-	-	-	-

Day	Lithium concentration ($mg\ell^{-1}$)	Volumetric flowrate (ℓ)	Lithium mass (mg)	Lithium cumulative mass (mg)
168	0.456	32	14.592	808.227
176	0.422	32	13.504	821.731
183	0.364	32	11.648	833.379
190	0.469	34	15.946	849.325
197	0.435	33	14.355	863.680
204	0.379	33	12.507	876.187
211	0.266	35	9.310	885.497
218	0.172	43	7.396	892.893
224	0.209	34	7.106	899.999
234	0.145	44	6.380	906.379
239	0.145	40	5.800	912.179
246	0.140	40	5.600	917.779
253	0.125	38	4.750	922.529
260	0.120	35	4.200	926.729
267	0.108	37	3.996	930.725
274	0.099	40	3.960	934.685
281	0.094	41	3.854	938.539
288	0.094	37	3.478	942.017
295	0.089	38	3.382	945.399
302	0.081	43	3.483	948.882
309	0.074	38	2.812	951.694
317	0.068	38	2.584	954.278
	Ave. flowrate	5.211 $Lday^{-1}$		

Note
Day 0 corresponds to Day 182 in the overall experiment
The initial mass of lithium sulphate added = 1027.7 mg

APPENDIX E

Results: co-disposal of copper, chromium and arsenic at pilot-scale

A solution of copper, chromium and are arsenic was added to Columns, 3 and 5. The leachate volumetric flowrates and analysis of the leachate are shown below.

Table E-1
Leachate volume and metal concentration: Column 3

Day (co-dis)	Volumetric flowrate (ℓ)	Copper ($mg\ell^{-1}$)	Chromium ($mg\ell^{-1}$)	Arsenic ($\mu g\ell^{-1}$)
0	23	0.05	0.00	17
7	18	0.08	0.03	14
14	20	0.11	0.01	23
21	18	0.07	0.01	19
29	17	0.06	0.01	20
35	18	0.07	0.01	21
42	18	0.03	0.02	22
50	22	0.03	0.02	28
56	19	0.03	0.01	33
63	19	0.09	0.02	51
71	17	0.05	0.02	46
77	18	0.05	0.02	140
84	18	0.03	0.03	263
91	24	0.05	0.04	131
98	20	0.02	0.04	190
105	20	0.03	0.03	487
112	18	0.03	0.04	501
121	19	0.03	0.04	828
128	18	0.04	0.04	990
135	20	0.04	0.04	1004
142	21	0.04	0.04	673
149	20	0.04	0.04	801
156	19	0.05	0.03	794
166	21	0.04	0.03	809
170	12	0.06	0.03	809
177	18	0.06	0.03	830
187	20	0.06	0.04	829
194	20	0.06	0.04	2022
202	19	0.06	0.04	2006
211	21	0.05	0.04	2023
220	21	0.04	0.03	2020
227	20	0.02	0.02	2013
235	20	0.08	0.03	1995

Table E-2
Leachate composition: Column 3

Day (co-dis)	pH	COD ($mg\ell^{-1}$)	Electrical conductivity (μSm^{-1})	Chloride ($mg\ell^{-1}$ as Cl^-)
0	6.9	-	503	920
7	6.8	1015	481	950
14	6.9	1120	538	980
21	6.7	1172	371	920
29	6.8	1005	434	920
35	7.0	1188	420	810
42	6.9	1140	544	920
50	6.9	1062	440	890
56	6.8	964	482	910
63	6.8	990	402	900
71	6.8	1091	585	830
77	6.8	1076	550	850
84	6.8	969	584	790
91	6.8	810	644	615
98	6.7	863	660	720
105	7.0	614	554	590
112	6.8	694	532	505
121	6.8	602	477	415
128	6.8	526	460	405
135	6.4	680	424	395
142	6.8	420	396	370
149	6.8	501	390	360
156	6.7	430	382	350
166	6.8	711	381	340
170	6.8	377	367	340
177	6.9	343	340	300
187	6.7	419	329	265
194	6.8	466	315	235
202	6.7	469	329	220
211	6.7	470	318	220
220	6.6	377	290	200
227	6.6	291	290	200
235	6.6	380	295	190

Table E-3
Leachate volume and metal concentration: Column 5

Day (co-dis)	Volumetric flowrate (ℓ)	Copper ($mg\ell^{-1}$)	Chromium ($mg\ell^{-1}$)	Arsenic ($\mu g\ell^{-1}$)
0	17	0.07	0.06	24
7	14	0.05	0.06	16
15	14	0.04	0.01	25
21	20	0.04	0.01	15
28	17	0.03	0.01	12
36	20	0.03	0.01	11
42	17	0.05	0.01	10
49	17	0.05	0.03	11
57	16	0.05	0.02	18
63	16	0.04	0.02	20
70	19	0.03	0.02	31
77	26	0.04	0.07	29
84	15	0.02	0.03	34
91	20	0.03	0.06	56
98	17	0.03	0.07	89
107	20	0.03	0.06	158
114	18	0.03	0.06	253
121	19	0.03	0.06	301
128	18	0.02	0.05	194
135	19	0.03	0.05	198
142	21	0.02	0.04	215
152	22	0.03	0.04	222
156	13	0.05	0.07	214
163	18	0.02	0.05	225
173	21	0.02	0.05	229
180	19	0.03	0.05	687
188	20	0.02	0.04	742
197	24	0.02	0.04	776
206	21	0.02	0.04	796
213	24	0.04	0.03	802
221	23	0.04	0.02	757

Table E-4
Leachate composition: Column 5

Day (co-dis)	pH	COD ($mg\ell^{-1}$)	Electrical conductivity (μSm^{-1})	Chloride ($mg\ell^{-1}$ as Cl^-)
0	7.0	1140	468	1000
7	6.8	1172	386	1010
15	6.9	1087	440	1010
21	6.9	1063	425	880
28	7.0	1080	449	1000
36	6.8	1113	476	940
42	6.9	1046	452	1020
49	6.9	1010	393	1005
57	6.9	1091	578	915
63	6.9	1259	524	915
70	6.9	1010	584	850
77	6.8	911	673	790
84	6.8	882	688	825
91	6.9	772	591	695
98	6.8	753	581	610
107	6.8	675	521	540
114	6.9	670	505	525
121	6.4	619	486	510
128	6.9	477	476	500
135	6.8	629	448	420
142	6.7	520	436	400
152	6.8	810	435	395
156	6.8	482	422	395
163	6.9	794	413	350
173	6.8	589	373	300
180	6.8	475	364	265
188	6.7	448	373	255
197	6.6	406	373	260
206	6.6	397	330	230
213	6.6	322	320	250
221	6.7	395	320	230

APPENDIX F

Table F-1
Copper adsorption and desorption at pH 5.5, 6.4 and 7.0

Coding	pH	Initial soln concn ($mg\ell^{-1}$)	Final soln concn ($mg\ell^{-1}$)	Mass sorbed (mg)	Initial soln concn ($mg\ell^{-1}$)	Final soln concn ($mg\ell^{-1}$)	Mass desorbed (mg)
A	5.5	63.6	8.8	54.8	0.2	2.6	2.4
B	5.5	53.2	8.4	44.8	0.2	1.5	1.3
C	5.5	65.1	11.9	53.2	0.1	1.7	1.6
Ave.	5.5	60.6	9.7	50.9	0.2	1.9	1.8
D	6.4	9.6	1.3	8.3	0.1	0.4	0.3
E	6.4	14.4	2.5	13.1	0.0	0.5	0.5
F	6.4	21.3	0.3	21.0	0.0	0.7	0.7
Ave.	6.4	15.1	1.0	14.1	0.0	0.5	0.5
G	7.0	30.8	3.5	27.3	0.1	0.8	0.7
H	7.0	22.1	2.9	19.2	0.1	1.0	0.9
I	7.0	27.4	5.0	22.4	0.1	0.9	0.8
Ave.	7.0	26.8	3.8	23.0	0.1	0.9	0.8

Table F-2
Chromium adsorption and desorption at pH 5.5, 6.4 and 7.0

Coding	pH	Initial soln concn ($mg\ell^{-1}$)	Final soln concn ($mg\ell^{-1}$)	Mass sorbed (mg)	Initial soln concn ($mg\ell^{-1}$)	Final soln concn ($mg\ell^{-1}$)	Mass desorbed (mg)
A	5.5	263	221	42	0.0	0.2	0.2
B	5.5	265	217	48	0.0	0.3	0.3
C	5.5	263	196	67	0.1	0.2	0.1
Ave.	5.5	264	211	53	0.0	0.2	0.2
D	6.4	269	234	35	0.0	0.2	0.2
E	6.4	262	230	32	0.0	0.2	0.2
F	6.4	259	232	27	0.0	0.2	0.2
Ave.	6.4	263	232	31	0.0	0.2	0.2
G	7.0	223	203	20	0.0	0.2	0.2
H	7.0	224	202	22	0.0	0.2	0.2
I	7.0	230	209	21	0.0	1.1	1.1
Ave.	7.0	226	205	21	0.0	0.5	0.5

Table F-3
Arsenic adsorption and desorption at pH 5.5, 6.4 and 7.0

Coding	pH	Initial soln concn ($mg\ell^{-1}$)	Final soln concn ($mg\ell^{-1}$)	Mass sorbed (mg)	Initial soln concn ($mg\ell^{-1}$)	Final soln concn ($mg\ell^{-1}$)	Mass desorbed (mg)
A	5.5	225	163	92	0	7	7
B	5.5	231	194	37	0	6	6
C	5.5	260	179	81	0	6	6
Ave.	5.5	249	179	70	6	6	6
D	6.4	228	187	41	0	4	4
E	6.4	225	191	34	0	3	3
F	6.4	231	197	34	0	4	4
Ave.	6.4	228	192	36	0	4	4
G	7.0	236	186	50	0	5	5
H	7.0	219	183	36	0	3	3
I	7.0	214	178	36	0	4	4
Ave.	7.0	223	182	40.7	0	4	4

APPENDIX G

The graphs below show the laboratory scale experimental data together with modelled curve

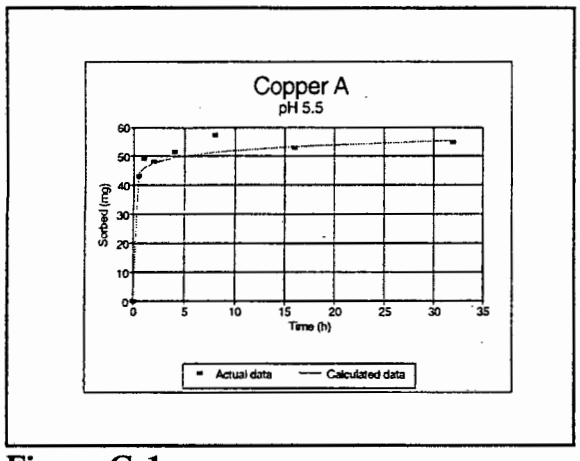

Figure G-1
Adsorption of copper A: pH 5.5

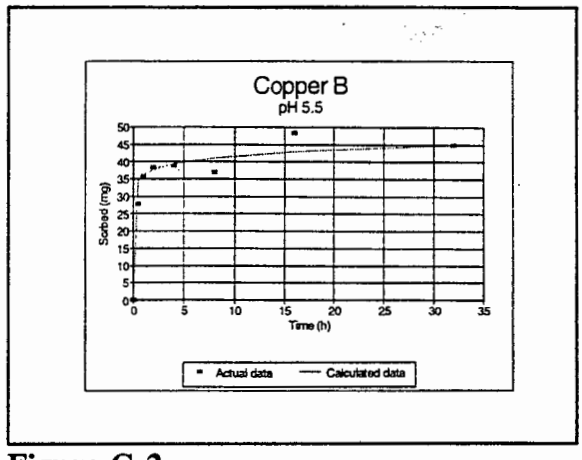

Figure G-2
Adsorption of copper B: pH 5.5

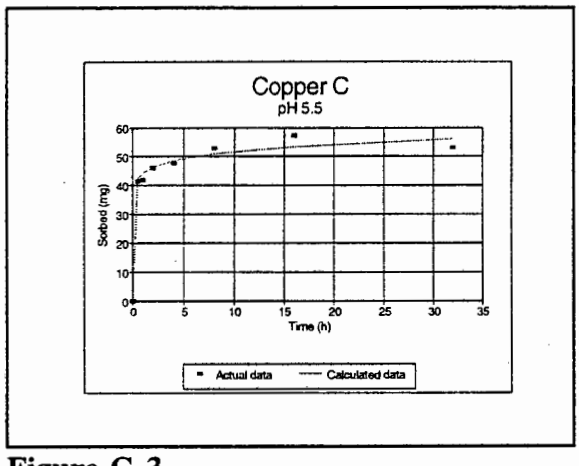

Figure G-3
Adsorption of copper C: pH 5.5

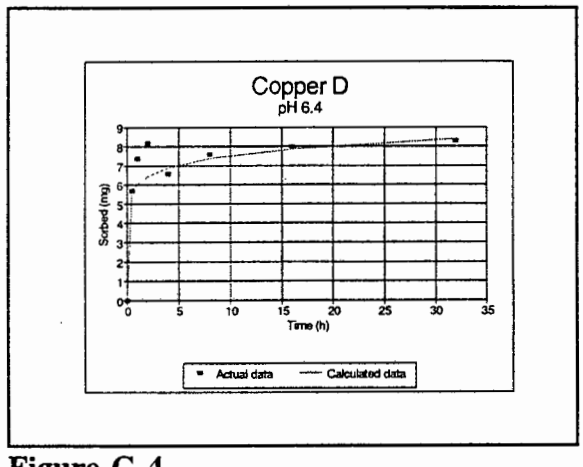

Figure G-4
Adsorption of copper D: pH 6.4

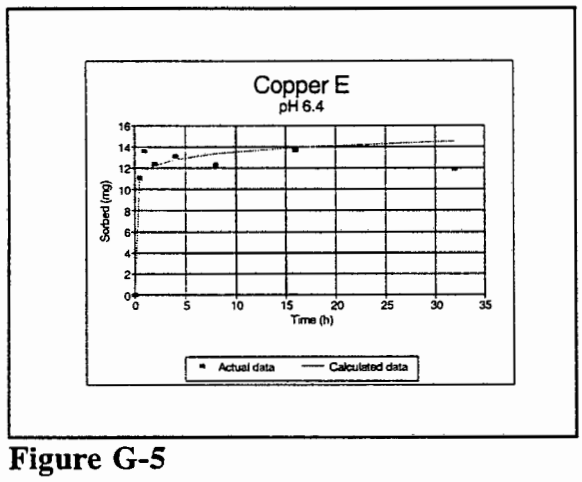

Figure G-5
Adsorption of copper E: pH 6.4

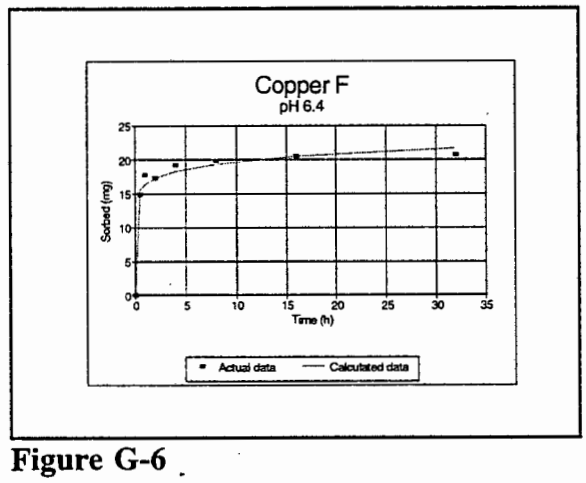

Figure G-6
Adsorption of copper F: pH 6.4

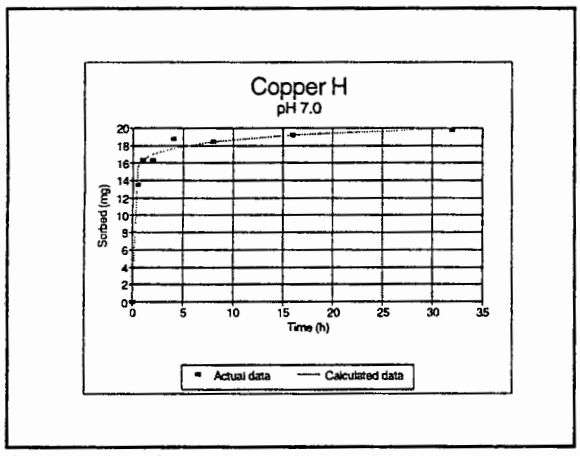

Figure G-7
Adsorption of copper G: pH 7.0

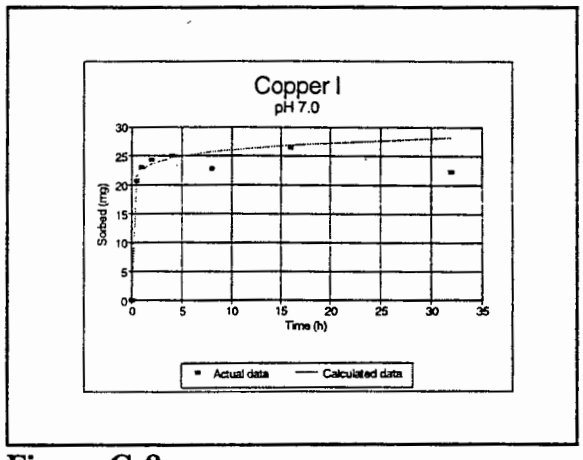

Figure G-8
Adsorption of copper I: pH 7.0

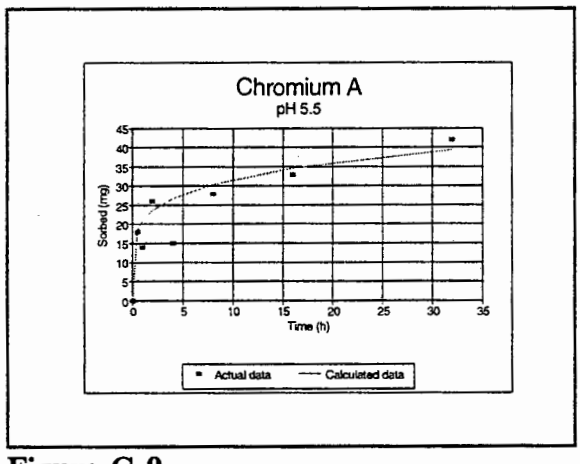

Figure G-9
Adsorption of chromium pH A: 5.5

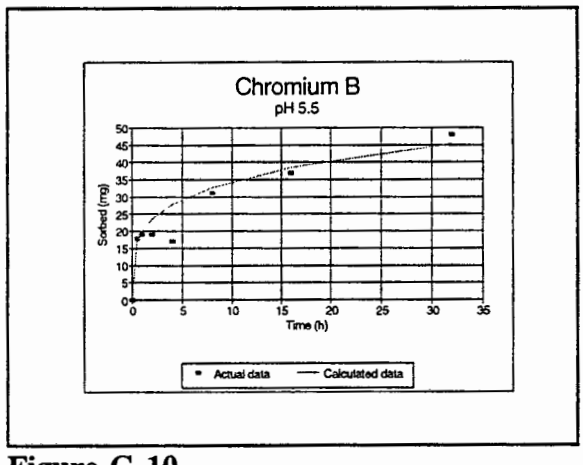

Figure G-10
Adsorption of chromium B: pH 5.5

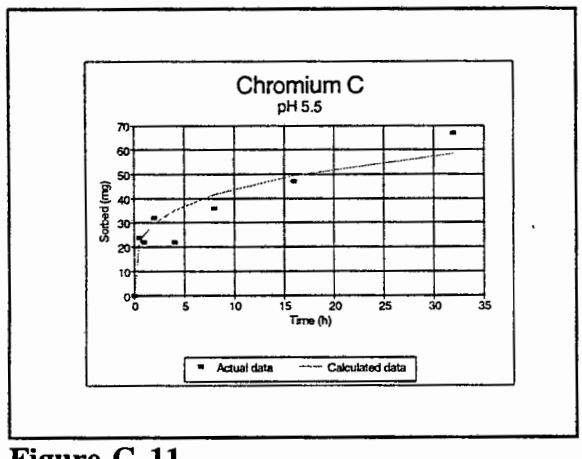

Figure G-11
Adsorption of chromium C: pH 5.5

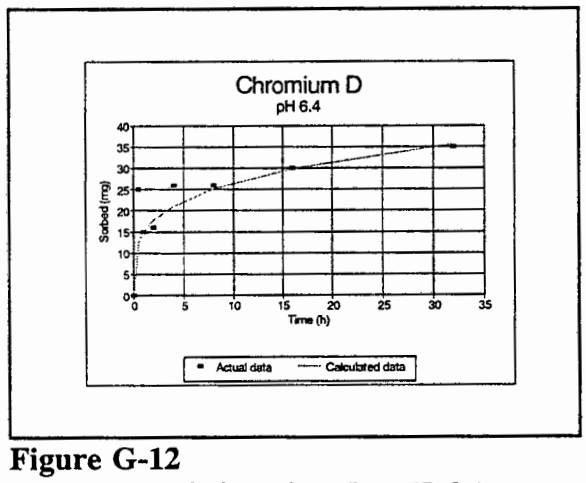

Figure G-12
Adsorption of chromium D: pH 6.4

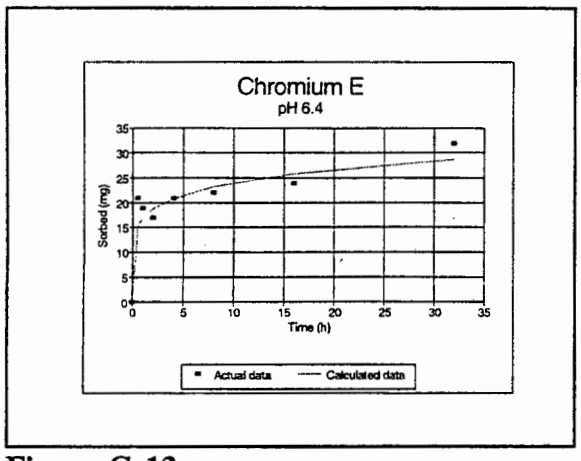

Figure G-13
Adsorption of chromium E: pH 6.4

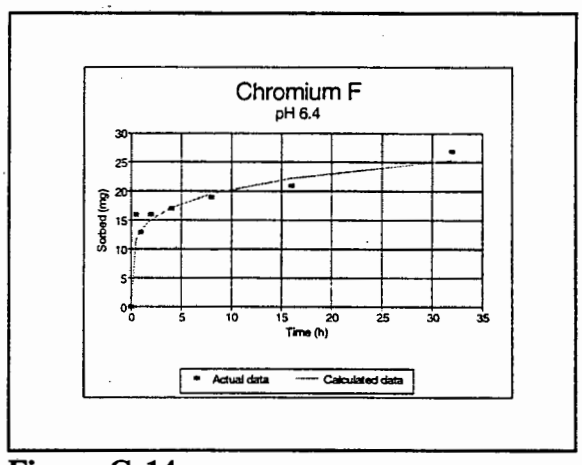

Figure G-14
Adsorption of chromium F: pH 7.0

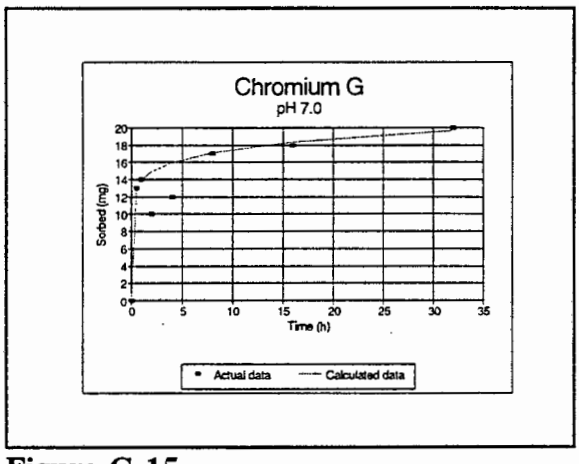

Figure G-15
Adsorption of chromium G: pH 7.0

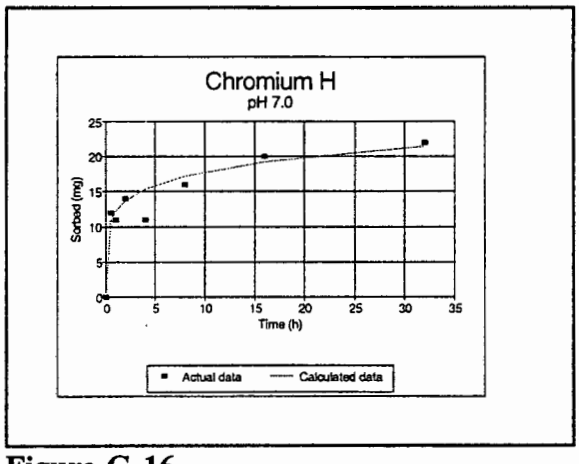

Figure G-16
Adsorption of chromium H: pH 7.0

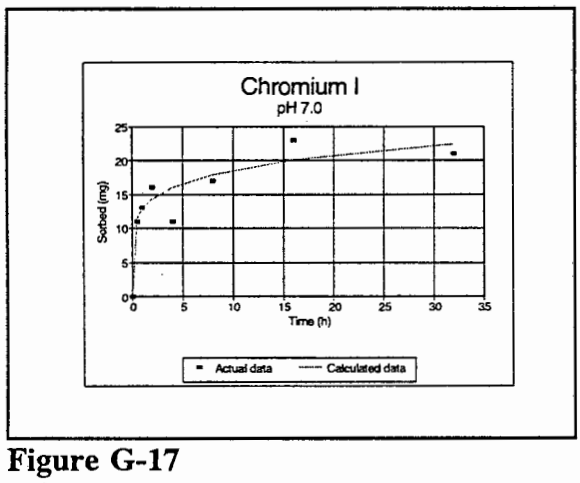

Figure G-17
Adsorption of chromium I: pH 7.0

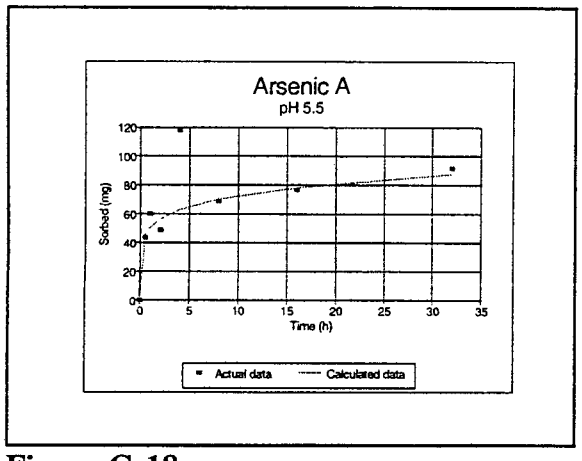

Figure G-18
Adsorption of arsenic A: pH 5.5

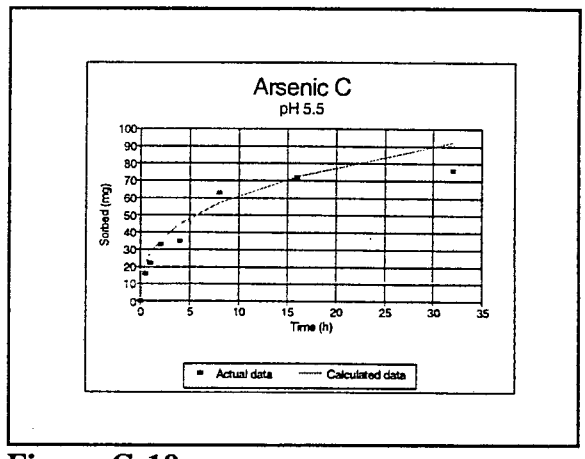

Figure G-19
Adsorption of arsenic C: pH 5.5

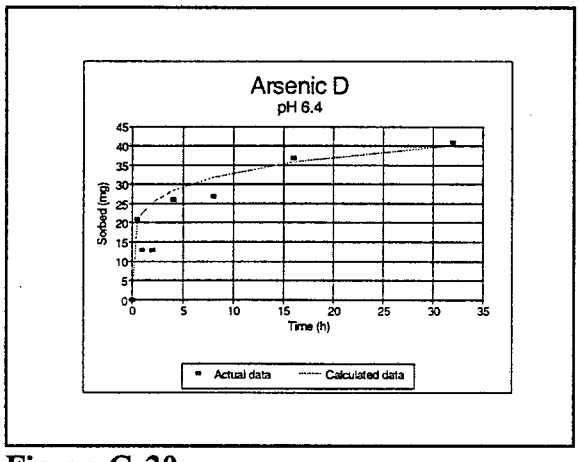

Figure G-20
Adsorption of arsenic D: pH 6.4

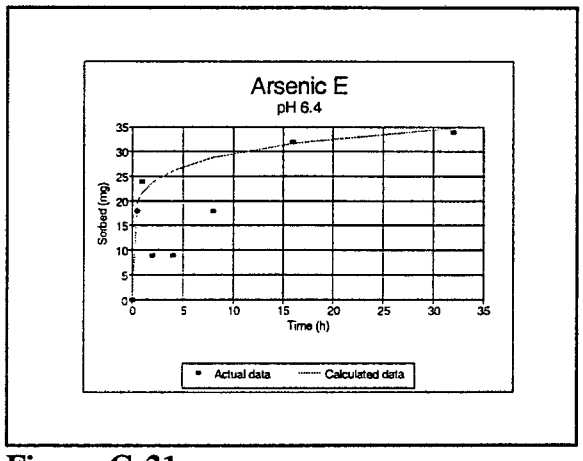

Figure G-21
Adsorption of arsenic E: pH 6.4

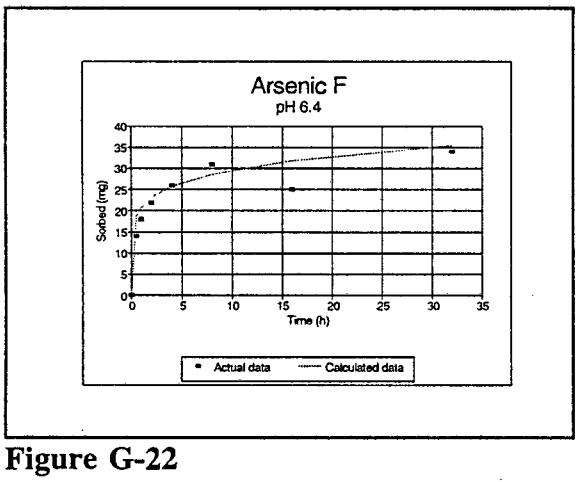

Figure G-22
Adsorption of arsenic F: pH 6.4

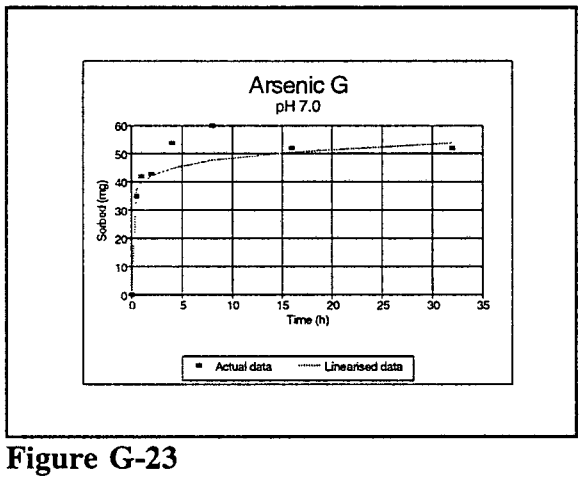

Figure G-23
Adsorption of arsenic G: pH 7.0

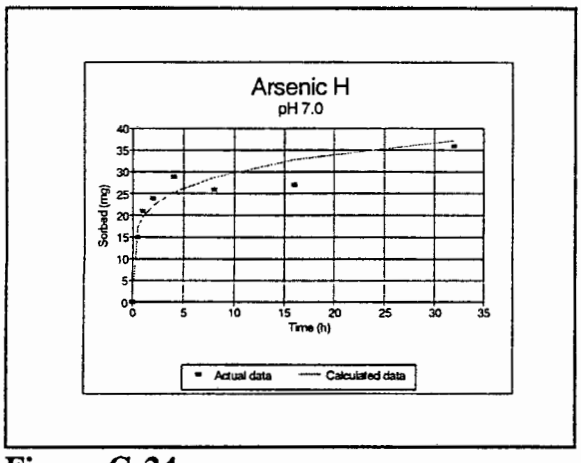

Figure G-24
Adsorption of arsenic H: pH 7.0

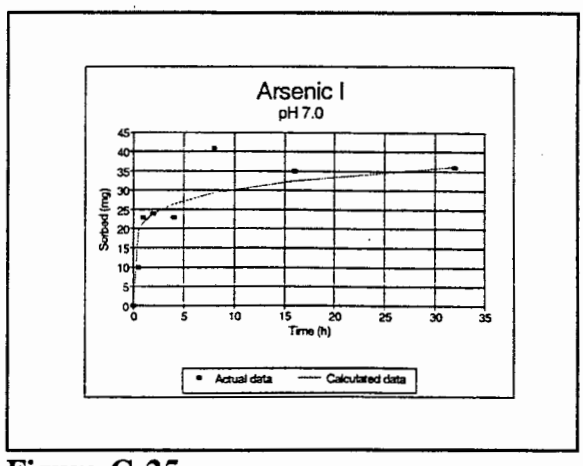

Figure G-25
Adsorption of arsenic I: pH 7.0

Table G-1
Regression analysis - tabulated results for copper

Coding	Maximum regression observations available	Utilised number of regression observations	Neglected observations @ t = z hours	R squared
A	7	5	1.0 8.0	0.94
B	7	4	0.5 8.0 16.0	0.98
C	7	6	16.0	0.90
D	7	5	1.0 2.0	0.96
E	7	4	1.0 8.0 32.0	0.95
F	7	6	1.0	0.92
H	7	6	0.5	0.85
I	7	5	8.0 32.0	0.90

Table G-2
Regression analysis - tabulated results for chromium

Coding	Maximum regression observations available	Utilised number of regression observations	Neglected observations @ t = z hours	R squared
A	7	5	1.0 4.0	0.94
B	7	4	2.0 4.0 8.0	0.99
C	7	6	4.0	0.91
D	7	6	0.5	0.92
E	7	6	0.5	0.82
F	7	6	0.5	0.96
G	7	5	2.0 4.0	0.99
H	7	6	4.0	0.93
I	7	6	4.0	0.90

Table G-3
Regression analysis - tabulated results for arsenic

Coding	Maximum regression observations available	Utilised number of regression observations	Neglected observations @ t = z hours	R squared
A	7	6	4.0	0.86
C	7	7	-	0.96
D	7	4	1.0 2.0 8.0	0.96
E	7	4	2.0 4.0 8.0	0.92
F	7	4	0.5 1.0 16.0	0.90
G	7	5	4.0 8.0	0.91
H	7	6	16.0	0.87
I	7	4	0.5 8.0	0.86

APPENDIX H

Table H-1
Tabulated calculations for the evaluation of the area, mean($\bar{t}$) and variance(σ^2): column 4

Time (days) [t]	Lithium mass {mg} [m]	Δt	m Δt	t m Δt	t^2 m Δt
0	1.122	0	0.00	0.0	0
7	1.190	7	8.33	58.3	408
14	1.404	7	9.83	137.6	1926
21	4.480	7	31.36	658.6	13830
29	10.915	8	87.32	2532.3	73436
35	12.648	6	75.89	2656.1	92963
42	20.054	7	140.38	5895.9	247627
49	24.831	7	173.82	8517.0	417335
56	38.502	7	269.51	15092.8	845196
63	47.508	7	332.56	20951.0	1319915
70	68.250	7	477.75	33442.5	2340975
77	73.112	7	511.78	39407.4	3034367
84	76.114	7	532.80	44755.0	3759423
92	70.980	8	567.84	52241.3	4806198
98	64.638	6	387.83	38007.1	3724700
106	57.080	8	456.64	48403.8	5130807
112	43.848	6	263.09	29465.9	3300176
119	38.012	7	266.08	31664.0	3768016
126	35.735	7	250.15	31518.3	3971302
134	25.092	8	200.74	26898.6	3604416
140	22.506	6	135.04	18905.0	2646706
147	21.216	7	148.51	21831.3	3209196
155	17.248	8	137.98	21387.5	3315066
161	17.150	6	102.90	16566.9	2667271
168	14.592	7	102.14	17160.2	2882912
176	13.504	8	108.03	19013.6	3346399
183	11.648	7	81.54	14921.1	2730559

Time (days) [t]	Lithium mass {mg} [m]	Δt	$m\ \Delta t$	$t\ m\ \Delta t$	$t^2\ m\ \Delta t$
190	15.946	7	111.62	21208.2	4029554
197	14.355	7	100.49	19795.5	3899722
204	12.507	7	87.55	17860.0	3643439
211	9.310	7	65.17	13750.9	2901434
218	7.396	7	51.77	11286.3	2460413
224	7.106	6	42.64	9550.5	2139304
234	6.380	10	63.80	14929.2	3493433
239	5.800	5	29.00	6931.0	1656509
246	5.600	7	39.20	9643.2	2372227
253	4.750	7	33.25	8412.3	2128299
260	4.200	7	29.40	7644.0	1987440
267	3.996	7	27.97	7468.5	1994096
274	3.960	7	27.72	7595.3	2081107
281	3.854	7	26.98	7580.8	2130210
288	3.478	7	24.35	7011.6	2019355
295	3.382	7	23.67	6983.8	2060230
302	3.483	7	24.38	7363.1	2223645
309	2.812	7	19.68	6082.4	1879448
317	2.584	8	20.67	6553.0	2077309
		$\sum m\ \Delta t =$	6709.1		
			$\sum t\ C\ \Delta t =$	759738.6	
				$\sum t^2\ C\ \Delta t =$	108428295

Table H-2
Calculated data for the evaluation of E(t), E and θ: column 4

Time (days) [t]	Lithium mass {mg} [m]	E(t) [vC/M]	E [E(t).t̄]	θ [t / .t̄]
0	1.122	0.0002	0.0189	0.0000
7	1.190	0.0002	0.0201	0.0618
14	1.404	0.0002	0.0237	0.1236
21	4.480	0.0007	0.0756	0.1854
29	10.915	0.0016	0.1842	0.2561
35	12.648	0.0019	0.2135	0.3091
42	20.054	0.0030	0.3385	0.3709
49	24.831	0.0037	0.4191	0.4327
56	38.502	0.0057	0.6499	0.4945
63	47.508	0.0071	0.8019	0.5563
70	68.250	0.0102	1.1519	0.6182
77	73.112	0.109	1.2340	0.6800
84	76.114	0.0113	1.2847	0.7418
92	70.980	0.0106	1.1980	0.8124
98	64.638	0.0096	1.0910	0.8654
106	57.080	0.0085	0.9634	0.9361
112	43.848	0.0065	0.7401	0.9891
119	38.012	0.0057	0.6416	1.0509
126	35.735	0.0053	0.6031	1.1127
134	25.092	0.0037	0.4235	1.1833
140	22.506	0.0034	0.3799	1.263
147	21.216	0.0032	0.3581	1.2981
155	17.248	0.0026	0.2911	1.3688
161	17.150	0.0026	0.2895	1.4218
168	14.592	0.0022	0.2463	1.4836
176	13.504	0.0020	0.2279	1.5542
183	11.648	0.0017	0.1966	1.6160

Time (days) [t]	Lithium {mg} [m]	E(t) [vC/M]	E [E(t).t̄]	θ [t / .t̄]
190	15.946	0.0017	0.2691	1.6779
197	14.355	0.0024	0.2423	1.7397
204	12.507	0.0021	0.2111	1.8015
211	9.310	0.0019	0.1571	1.8633
218	7.396	0.0014	0.1248	1.9251
224	7.106	0.0011	0.1199	1.9781
234	6.380	0.0011	0.1077	2.0664
239	5.800	0.0010	0.0979	2.1106
246	5.600	0.0009	0.0945	2.1724
253	4.750	0.0008	0.0802	2.2342
260	4.200	0.0007	0.0709	2.2960
267	3.996	0.0006	0.0674	2.3578
274	3.960	0.0006	0.0668	2.4197
281	3.854	0.0006	0.0650	2.4815
288	3.478	0.0006	0.0587	2.5433
295	3.382	0.0005	0.0571	2.6051
302	3.483	0.0005	0.0588	2.6669
309	2.812	0.0005	0.0475	2.7287
317	2.584	0.0004	0.0436	2.7994

APPENDIX I

Table I-1
Predicted results for Column 3: residence time distribution

Day	Li conc	Vol flow	Li mass	E(t)	E	θ	Incremental E
0	0.034	33	1.122	0.0001	0.0189	0.0000	0.0000
13.2	0.035	34	1.190	0.0001	0.0201	0.0618	0.0012
26.5	0.052	27	1.404	0.0001	0.0237	0.1236	0.0015
39.7	0.140	32	4.480	0.0004	0.0756	0.1854	0.0047
54.9	0.295	37	10.915	0.0009	0.1842	0.2561	0.0130
66.2	0.372	34	12.648	0.0010	0.2135	0.3091	0.0113
79.5	0.542	37	20.054	0.0016	0.3385	0.3709	0.0209
92.7	0.801	31	24.831	0.0020	0.4191	0.4327	0.0259
106.0	1.242	31	38.502	0.0030	0.6499	0.4945	0.0402
119.2	1.284	37	47.508	0.0037	0.8019	0.5563	0.0496
132.5	1.950	35	68.250	0.0054	1.1519	0.6182	0.0712
145.7	1.976	37	73.112	0.0058	1.2340	0.6800	0.0763
159.0	2.003	38	76.114	0.0060	1.2847	0.7418	0.0794
174.1	1.820	39	70.980	0.0056	1.1980	0.8124	0.0846
185.4	1.701	38	64.638	0.0051	1.0910	0.8654	0.0578
200.6	1.427	40	57.080	0.0045	0.9634	0.9361	0.0681
211.9	1.218	36	43.848	0.0035	0.7401	0.9891	0.0392
225.2	1.118	34	38.012	0.0030	0.6416	1.0509	0.0397
238.4	1.021	35	35.735	0.0028	0.6031	1.1127	0.0373
253.6	0.697	36	25.092	0.0020	0.4235	1.1833	0.0299
264.9	0.682	33	22.506	0.0018	0.3799	1.2363	0.0201
278.2	0.624	34	21.216	0.0017	0.3581	1.2981	0.0221
293.3	0.539	32	17.248	0.0014	0.2911	1.3688	0.0206
304.7	0.490	35	17.150	0.0014	0.2895	1.4218	0.0153
317.9	0.456	32	14.592	0.0011	0.2463	1.4836	0.0152

Day	Li conc	Vol flow	Li mass	E(t)	E	θ	Incremental E
333.0	0.422	32	13.504	0.0011	0.2279	1.5542	0.0161
346.3	0.364	32	11.648	0.0009	0.1966	1.6160	0.0122
359.5	0.469	34	15.946	0.0013	0.2691	1.6779	0.0166
372.8	0.435	33	14.355	0.0011	0.2423	1.7397	0.0150
386.0	0.379	33	12.507	0.0010	0.2111	1.8015	0.0130
399.3	0.266	35	9.310	0.0007	0.1571	1.8633	0.0097
412.5	0.172	43	7.396	0.0006	0.1248	1.9251	0.0077
423.9	0.209	34	7.106	0.0006	0.1199	1.9781	0.0064
442.8	0.145	44	6.380	0.0005	0.1077	2.0664	0.0095
452.3	0.145	40	5.800	0.0005	0.0979	2.1106	0.0043
465.5	0.140	40	5.600	0.0004	0.0945	2.1724	0.0058
478.8	0.125	38	4.750	0.0004	0.0802	2.2342	0.0050
492.0	0.120	35	4.200	0.0003	0.0709	2.2960	0.0044
505.2	0.108	37	3.996	0.0003	0.0674	2.3578	0.0042
518.5	0.099	40	3.960	0.0003	0.0668	2.4197	0.0041
531.7	0.094	41	3.854	0.0003	0.0650	2.4815	0.0040
545.0	0.094	37	3.478	0.0003	0.0587	2.5433	0.0036
558.2	0.089	38	3.382	0.0003	0.0571	2.6051	0.0035
571.5	0.081	43	3.483	0.0003	0.0588	2.6669	0.0036
584.7	0.074	38	2.812	0.0002	0.0475	2.7287	0.0029
599.9	0.068	38	2.584	0.0002	0.0436	2.7994	0.0031

Table I-2
Predicted for column 3: tabulated calculations for the evaluation of the area, mean($\bar{t}$) and variance(σ^2)

Time (days) [t]	Lithium mass {mg} [m]	Δt	m Δt	t m Δt	t^2 m Δt
0	1.122	0	0.00	0.0	0
13.2	1.190	13.2	15.76	208.8	2766
26.5	1.404	13.2	18.60	492.7	13052
39.7	4.480	13.2	59.34	2358.2	93710
54.9	10.915	15.1	165.24	9067.6	497601
66.2	12.648	11.4	143.60	9510.9	629913
79.5	20.054	13.2	265.64	21112.0	1677911
92.7	24.831	13.2	328.91	30497.9	2827846
106.0	38.502	13.2	510.00	54044.4	5757021
119.2	47.508	13.2	629.30	75021.6	8943702
132.5	68.250	13.2	904.05	119751.1	15862374
145.7	73.112	13.2	968.45	141110.2	20560779
159.0	76.114	13.2	1008.21	160259.1	25473732
174.1	70.980	15.1	1074.52	187066.0	32566648
185.4	64.638	11.4	733.89	136096.3	25238453
200.6	57.080	15.1	864.10	173324.8	34766190
211.9	43.848	11.4	497.84	105511.6	22361890
225.2	38.012	13.2	503.51	113382.7	25531957
238.4	35.735	13.2	473.35	112860.9	26909240
253.6	25.092	15.1	379.85	96318.8	24423409
264.9	22.506	11.4	255.53	67695.3	17933995
278.2	21.216	13.2	281.03	78173.5	21745412
293.3	17.248	15.1	261.11	76584.6	22462782
304.7	17.150	11.4	194.72	59322.9	18073345
317.9	14.592	13.2	193.29	61447.3	19534524
333.0	13.504	15.1	204.43	68084.2	22675098
346.3	11.648	13.2	154.29	53429.5	18502184

Time (days) [t]	Lithium {mg} [m]	Δt	$m\ \Delta t$	$t\ m\ \Delta t$	$t^2\ m\ \Delta t$
359.5	15.946	13.2	211.22	75942.4	27304135
372.8	14.355	13.2	190.15	70884.0	26424398
386.0	12.507	13.2	165.67	63953.2	24687831
399.3	9.310	13.2	123.32	49239.2	19660024
412.5	7.396	13.2	97.97	40414.1	16671679
423.9	7.106	11.4	80.68	34198.4	14495857
442.8	6.380	18.9	120.73	53458.6	23671393
452.3	5.800	9.5	54.88	24818.6	11224454
465.5	5.600	13.2	74.18	34530.4	16074138
478.8	4.750	13.2	62.92	30122.6	14421290
492.0	4.200	13.2	55.63	27371.7	13466832
505.2	3.996	13.2	52.93	26743.3	13511932
518.5	3.960	13.2	52.45	27197.2	14101515
531.7	3.854	13.2	51.05	27145.4	14434236
545.0	3.478	13.2	46.07	25107.4	13683085
558.2	3.382	13.2	44.80	25007.7	13960054
571.5	3.483	13.2	46.14	26365.7	15067348
584.7	2.812	13.2	37.25	21779.7	12735082
599.9	2.584	15.1	39.12	23465.1	14075779
		$\sum m\ \Delta t =$	12695.7		
			$\sum t\ C\ \Delta t =$	2720477.6	
				$\sum t^2\ C\ \Delta t =$	734706779

APPENDIX J

COMPUTATIONAL METHOD - CHROMIUM CONCENTRATION IN REACTOR EFFLUENT (LEACHATE)

The initial step of the calculation is to determine a suitable increment of depth. The total depth of the column is 1940mm. The kinetics of the metals show an initial rapid sorption, with a decreasing sorption rate, at larger values of time, as equilibrium is neared. It therefore of importance that the elements of fluid do not exceed the time required to reach equilibrium, in each increment of depth. In the trial stages increments of depth of 100mm and 50mm was tried. The results obtained did not reflect the results obtained from the pilot-scale co-disposal trials. The depth was therefore minimised to 20mm. This was found to be satisfactory.

The **E**(t) curve allows the calculation of the mass fraction of liquid flowing in any designated time increment. This is a simple geometric application. The area of each increment is calculated by multiplying the **E**(t) value by the mean of the relevant time increment. The accuracy of this calculation can be ascertained, as the area under the **E**(t) curve must equal 1.00. It is assumed that the liquid carries an equal proportion of the co-disposed waste. The initial mass of chromium flowing in any time increment may be calculated and is designated CAo. CAo is then determined as mass of chromium per mass of waste in that increment. These initial computations are shown below.

Relevant data

Mass of chromium co-disposed	=	256.1g
Mass of MSW in column	=	668kg
Depth of MSW	=	1940mm
Depth of increment	=	20mm

Then,

Mass of MSW per increment	=	(668/1940) × 20	=	6.887kg

Consider the first increment,

Incremental **E**(t)	=	(13.2 - 0.0) × 0.0001	=	0.0012
CAo	=	256.1 × 0.0012/6.886	=	0.0462
Average day	=	(13.2 + 0.0)/2	=	6.6

Consider the second increment,

Incremental **E**(t)	=	(26.5 - 13.2) × 0.0001	=	0.00146
CAo	=	256.1 × 0.00146/6.886	=	0.0545
Average day	=	(26.5 + 13.2)/2	=	19.9

These calculations are now completed for the entire residence time of the fluid in the column, and are shown below in Table J-1

Table J-1
Predicted results for Column 3: residence time distribution

Day	Li conc	Vol flow	Li mass	E(t)	Incre-mental E(t)	CAo	Day (Ave)
0	0.034	33	1.122	0.0001	0.0000	0.000	
13.2	0.035	34	1.190	0.0001	0.0012	0.046	6.6
26.5	0.052	27	1.404	0.0001	0.0015	0.055	19.9
39.7	0.140	32	4.480	0.0004	0.0047	0.174	33.1
54.9	0.295	37	10.915	0.0009	0.0130	0.484	47.3
66.2	0.372	34	12.648	0.0010	0.0113	0.421	60.6
79.5	0.542	37	20.054	0.0016	0.0209	0.778	72.9
92.7	0.801	31	24.831	0.0020	0.0259	0.964	86.1
106.0	1.242	31	38.502	0.0030	0.0402	1.494	99.3
119.2	1.284	37	47.508	0.0037	0.0496	1.843	112.6
132.5	1.950	35	68.250	0.0054	0.0712	2.648	125.8
145.7	1.976	37	73.112	0.0058	0.0763	2.837	139.1
159.0	2.003	38	76.114	0.0060	0.0794	2.953	152.3
174.1	1.820	39	70.980	0.0056	0.0846	3.148	166.5
185.4	1.701	38	64.638	0.0051	0.0578	2.150	179.8
200.6	1.427	40	57.080	0.0045	0.0681	2.531	193.0
211.9	1.218	36	43.848	0.0035	0.0392	1.458	206.3
225.2	1.118	34	38.012	0.0030	0.0397	1.475	218.6
238.4	1.021	35	35.735	0.0028	0.0373	1.387	231.8
253.6	0.697	36	25.092	0.0020	0.0299	1.113	246.0
264.9	0.682	33	22.506	0.0018	0.0201	0.749	259.2
278.2	0.624	34	21.216	0.0017	0.0221	0.823	271.5
293.3	0.539	32	17.248	0.0014	0.0206	0.765	285.7
304.7	0.490	35	17.150	0.0014	0.0153	0.570	299.0
317.9	0.456	32	14.592	0.0011	0.0152	0.566	311.3

Day	Li conc	Vol flow	Li mass	E(t)	Incre-mental E	CAo	Day (Ave)
333.0	0.422	32	13.504	0.0011	0.0161	0.599	325.5
346.3	0.364	32	11.648	0.0009	0.0122	0.452	339.7
359.5	0.469	34	15.946	0.0013	0.0166	0.619	352.9
372.8	0.435	33	14.355	0.0011	0.0150	0.557	366.2
386.0	0.379	33	12.507	0.0010	0.0130	0.485	379.4
399.3	0.266	35	9.310	0.0007	0.0097	0.361	392.7
412.5	0.172	43	7.396	0.0006	0.0077	0.287	405.9
423.9	0.209	34	7.106	0.0006	0.0064	0.236	418.2
442.8	0.145	44	6.380	0.0005	0.0095	0.354	433.4
452.3	0.145	40	5.800	0.0005	0.0043	0.161	447.6
465.5	0.140	40	5.600	0.0004	0.0058	0.217	458.9
478.8	0.125	38	4.750	0.0004	0.0050	0.184	472.1
492.0	0.120	35	4.200	0.0003	0.0044	0.163	485.4
505.2	0.108	37	3.996	0.0003	0.0042	0.155	498.6
518.5	0.099	40	3.960	0.0003	0.0041	0.154	511.9
531.7	0.094	41	3.854	0.0003	0.0040	0.150	525.1
545.0	0.094	37	3.478	0.0003	0.0036	0.135	538.4
558.2	0.089	38	3.382	0.0003	0.0035	0.131	551.6
571.5	0.081	43	3.483	0.0003	0.0036	0.135	564.9
584.7	0.074	38	2.812	0.0002	0.0029	0.109	578.1
599.9	0.068	38	2.584	0.0002	0.0031	0.115	592.3
Total					1.000		

The next phase in the computation is the application of the data generated from the kinetic trials. The computation utilises data from the trial designated Chromium H.

Relevant data

K_a	=	sorption rate coefficient (day^{-1})	=	0.0916
1/m	=	constant	=	0.1622
CAmax	=	Maximum sorption (gkg^{-1})	=	0.42

The calculation involves the use of interactive spreadsheets. Each time increment is computed separately. The time increments of 6.6 days and 19.9 days are shown below in Tables J-2 and J-3 respectively, to a depth of 100mm. The following nomenclature are employed.

CA_n = Initial chromium concentration
CA_{n+1} = Exiting chromium concentration
Max $\triangle CA$ = Calculated adsorption
Actual $\triangle CA$ = Allowable adsorption
= Maximum adsorption - Cumulative adsorption

Time increment = 6.6days
Duration of fluid in increment = 6.6/1940 × 20 = 0.068days

Table J-2
Calculation for time increment 6.6days

Increment (mm)	Time in increment (days)	CA_n	K_a	Max $\triangle CA$	Actual $\triangle CA$	CA_{n+1}
0 - 20	0.068	0.0462	0.0916	0.0027	0.0027	0.0434
20 - 40	0.068	0.0434	0.0916	0.0026	0.0026	0.0409
40 - 60	0.068	0.0409	0.0916	0.0024	0.0024	0.0384
60 - 80	0.068	0.0384	0.0916	0.0023	0.0023	0.0362
80 - 100	0.068	0.0362	0.0916	0.0021	0.0021	0.0340

Time increment = 19.9days
Duration of fluid in increment = 19.9/1940 × 20 = 0.205

Table J-3
Calculation for time increment 19.9 days

Increment (mm)	Time in increment (days)	CA_n	K_a	Max $\triangle CA$	Actual $\triangle CA$	CA_{n+1}
0 - 20	0.205	0.0545	0.0916	0.0039	0.0039	0.0506
20 - 40	0.205	0.0506	0.0916	0.0036	0.0036	0.0470
40 - 60	0.205	0.0470	0.0916	0.0033	0.0033	0.0437
60 - 80	0.205	0.0437	0.0916	0.0031	0.0031	0.0406
80 - 100	0.205	0.0406	0.0916	0.0029	0.0029	0.0377

The calculated adsorption is compared with the preceding cumulative adsorption in Table J-4 (i.e adsorption at 19.9 days is determined by the degree of metal deposited after 6.6 days. The maximum allowable adsorption is $0.42 gkg^{-1}$. The chromium may be fully adsorbed, partially adsorbed, or no adsorption may take place if the maximum allowable chromium concentration in that increment has been attained. The increase in chromium content in the incremental layers after 19.9 days can be clearly seen.

Table J-4
Cumulative chromium content of each incremental layer of depth

Increment (mm)	6.6 days	Cumulative	19.9 days	Cumulative
0 - 20	0.0027	0.0027	0.0039	0.0066
20 - 40	0.0026	0.0026	0.0036	0.0062
40 - 60	0.0024	0.0024	0.0033	0.0057
60 - 80	0.0023	0.0023	0.0031	0.0054
80 - 100	0.0021	0.0021	0.0029	0.0050

The calculation is continued in this manner to the final time increment of 592.3 days. The method of computation allows results to be reported in terms of metal saturation with depth and time. The final phase of the computation is the conversion of the final value of CA_{n+1} from a value based on the mass of solid in an increment. The mass of chromium can be easily calculated; the volume of leachate occurring in that time increment is known; the chromium concentration in leachate can be readily calculated.